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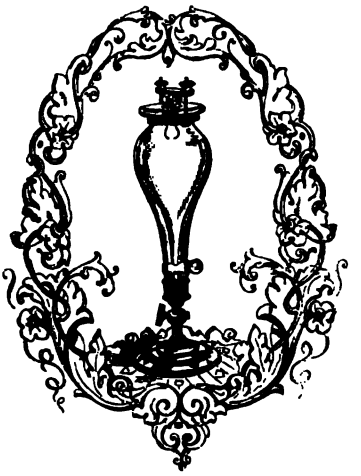

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# HAND-BOOK

OF

# CHEMISTRY.

BY

LEOPOLD GMELIN,

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF HEIDELBERG.
AND MEMBER OF VARIOUS LEARNED SOCIETIES IN BERLIN, BONN, CATANIA, DRESDEN, FREIBURG, FRANKFORT, GÖTTINGEN, HALLE, HAMBURG, HANAU, HEIDELBERG, JASSY, LONDON, MARBURG, MUNICH, PARIS, PETERSBURGH, VIENNA, AND WETTERAU.

VOL. III.

## METALS.

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# INORGANIC CHEMISTRY

(*Continued.*)

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SECOND SUBDIVISION.

## METALS.

THE *Metallic Elements* or *Pure Metals* are solid at ordinary temperatures, with the exception of Mercury, which is liquid—never gaseous: they are all however fusible, and for the most part volatile at high temperatures. Their specific gravity lies between 0·800 and 22·000. Some of the metals are brittle, and are known as the *Brittle Metals* or *Semimetals;* others yield, without breaking, to the blow of a hammer or to pressure, and may be formed into plates or drawn out into wire by mechanical means: these are the *Malleable* or *Perfect* Metals, *Extensible* and *Ductile Metals.* Their crystalline forms belong, some to the regular, others to the rhombohedral system. The metals, if not absolutely opaque (since gold in very fine laminæ is translucent) are yet the most impervious to light of all known bodies; they are distinguished also by a peculiar lustre connected with their opacity, which only disappears when they are reduced to a state of fine powder, and is again restored by pressure with the burnishing steel, which produces a continuous surface; they are also the best conductors of heat and electricity.

All the metals unite with oxygen, the combination being sometimes attended with development of light and heat: when thus combined, they generally lose their metallic lustre. From this union with oxygen there are produced—besides several suboxides and peroxides—a great number of salifiable bases, and likewise a few acids, for the most part not very powerful. Some of the metals when oxidized retain their oxygen with but a feeble affinity, and at a somewhat elevated temperature give it off completely in the state of gas;—*Noble Metals, reducible by heat alone;*—others retain it much more powerfully, and, to whatever temperature they may be heated, either give up no oxygen at all, or only a part of that with which they are combined, so that their reduction to a *regulus* or to the metallic state, can only be effected by ignition with charcoal or some other combustible substance:—*Base metals, not reducible by heat alone.*

The number of metals hitherto discovered amounts to 49 (or 51, if Niobium and Ilmenium be included); they may be arranged in the following groups:

A. Light Metals. The specific gravity of these metals lies, as far as is yet known, between 0·860 and 5·000.—These metals possess a remarkably strong affinity for oxygen, many of them rapidly decomposing water at ordinary temperatures. Their compounds with oxygen generally play the part of salifiable bases; one only has a more acid character, and a few are either peroxides or suboxides.

The Light Metals are:

*a. Alkali-Metals.* Those namely by whose union with oxygen are formed the *Alkalis* mentioned at page 4, Vol. II., and distinguished from Ammonia or the volatile alkali, by being *fixed* or *permanent in the fire.* They decompose water, even at 0°, with great violence.—Potassium, Sodium, Lithium, Barium, Strontium, and Calcium.

*b. Earth-Metals.* So called because with oxygen they generate the *Earths* (II., 4); these metals slowly decompose water at ordinary temperatures, and for the most part with ease, when aided by heat or by the addition of an acid.—Magnesium, Cerium, Lanthanum, Didymium, Yttrium, Erbium, Terbium, Glucinum, Aluminum, Thorinum, Zirconium, and Silicium.

B. Heavy Metals. The specific gravity of these metals lies between 5·308 and 22·000; some of them are brittle, others malleable; their melting points differ considerably. Some are capable of separating oxygen even from its combinations with the light metals, whilst others manifest but little affinity for that element.—Their oxygen compounds are either *Heavy Salifiable oxides,* (see Vol. II., pp. 39, 40) or *Metallic Acids, Suboxides* and *Peroxides.*

The Heavy Metals are:

*a. Base Metals not reducible by heat alone:* these are,

*α. Brittle,* and also

*α α. Difficultly fusible.*—Titanium, Tantalum, Niobium, Pelopium, Tungsten, Molybdenum, Vanadium, Chromium, Uranium, and Manganese.

*ϛ ϛ. Easily fusible* or *Volatile.*—Arsenic, Antimony, Tellurium, and Bismuth.

*ϛ. Malleable.*—Zinc, Cadmium, Tin, Lead, Iron, Cobalt, Nickel, and Copper.

*b. Noble Metals, reducible by heat alone.*—Mercury, Silver, Gold, Platinum, Palladium, Rhodium, Iridium, Ruthenium, and Osmium.

CHAPTER I.

# POTASSIUM.

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On the reduction of the Alkaline and Earthy Metals:
Sir Humphry Davy. *Phil. Transact.* 1808, 1; also *Gib.* 31, 113; also *N. Gehl.* 7, 595.—*Phil. Transact.* 1808, 333; also *N. Gehl.* 9, 484; also *Gilb.* 32, 365; 33, 257.—*Phil. Transact.* 1809, 39; also *Schw.* 1, 302 & 324; also *Gilb.* 35, 151, and 36, 180.—*Phil. Transact.* 1810, 16; also *Schw.* 3, 334; also *Gilb.* 37, 35.
—— On the Metals of the Earths. *Gilb.* 37, 186.
Gay-Lussac & Thénard. *Recherches physico-chimiques*, 1, 74 to 386.—Further: *N. Gehl.* 5, 703; also *Gilb.* 29, 135.—Further: *Gilb.* 32, 23.
Controversy between Davy & Gay-Lussac & Thénard. *Schw.* 1, 331; also *Gilb.* 35, 179;—*Gilb.* 36, 204;—*Gilb.* 36, 217;—*Schw.* 1, 338; also *Gilb.* 36, 222; and *Gilb.* 36, 232.
Berzelius & Pontin. *Gilb.* 36, 247.
Berzelius. *Gilb.* 37, 416.
Erman & Simon. *Gilb.* 28, 121.
Von Jacquin, Gruner, Erman & Simon, Seebeck & Ritter. *Gilb.* 28, 329 to 372.
Curaudau. *Ann. Chim.* 66, 97; also *Gilb.* 29, 85; also *N. Gehl.* 5, 699.
Trommsdorff. *Gilb.* 30, 330.
Tennant. *Ann. Chim.* 93, 291.
Sementini. *Gilb.* 47, 225.
Lampadius. *Schw.* 34, 221.
Brunner. *Bibl. Univ.* 22, 36; also *Schw.* 38, 517.
Wöhler. *Pogg.* 4, 23 & 474.
Serullas. *Ann. Chim. Phys.* 21, 201.
Mantell. *Ann. Phil.* 22, 232.
Pleischl. *Zeitschw. Phys. v. W.* 2, 307 & 343; 3, 326.
Schädler. *Ann. Pharm.* 20, 2.

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*Kalium, Kalimetall, Kalibasis;* improperly; *Hydruret of Potash, Kalihydrür.*

*History.* The term *Alkali* was applied by the Arabians to the carbonate of soda found in the ashes of marine plants. The same appellation was afterwards extended to carbonate of ammonia, and likewise to the carbonate of potash found in the ashes of land plants, which was long considered as identical with carbonate of soda. It was soon discovered that these three alkaline carbonates are rendered much more caustic by contact with lime; and hence the *Mild* (*i. e.* carbonated) alkalis were distinguished from the *Caustic* (*i. e.* pure) alkalis. Black, in 1756, showed that this change is due to the abstraction of carbonic acid from the mild alkalis by the action of the lime; and the theory afterwards proposed by Meyer, in 1764—who supposed that the burnt lime imparted to the

mild alkalis a peculiar principle of causticity, the so-called *Acidum pingue*—was quickly refuted and abandoned.—The older chemists distinguished ammonia, as the *Volatile Alkali*, from the two *Fixed Alkalis;* and of these—after their differences had been pointed out by Duhamel in 1736, and Marggraf in 1758—potash received the name of *Vegetable Alkali*, soda that of *Mineral Alkali*, inasmuch as potash was found chiefly in plant-ashes, soda in rock-salt. But Klaproth showed that potash exists in many widely diffused minerals, and consequently that the name of *Vegetable Alkali* cannot properly be applied to it. Accordingly, the term *Kali* was, at his suggestion, adopted in Germany to designate this substance. The French, on the other hand, invented the word *Potasse** to distinguish the pure alkali, deriving the term from the German word *Pottasche*, which probably owes its origin to the use of iron pots in burning the materials from which the alkali is obtained.—The alkalis and earths were long regarded as simple substances, although Lavoisier had suggested that they were metallic oxides, while others had supposed that they contained nitrogen, and Tondi and others, by subjecting the earths to strong ignition in contact with charcoal, thought that they obtained metallic globules,—which, however, appear to have been chiefly formed from the iron contained in the ingredients and in the crucible. Sir Humphry Davy, in 1807, first succeeded, by means of a powerful voltaic battery, in separating the metals from potash, soda, baryta, strontia, and lime, and in obtaining traces of metallization from the earths. The experiments of Davy were confirmed and extended by Gay-Lussac & Thénard, (who, for a while, regarded these metals as compounds of the alkalis with hydrogen) and by Berzelius. The discovery of these metals also led to that of pure potash and soda; for up to that time, these substances were known only in the state of hydrates, and these hydrates were long regarded as anhydrous alkalis.

*Sources.* As sulphate of potash in alum, alum-stone, and polyhalite; as nitrate on the surface of the earth; as silicate, united with the earths in various minerals, especially in apophyllite, potash-harmotome, chabasite, pearlstone, pumicestone, obsidian, felspar, leucite, mica, lepidolite, schorl, haüyne, pinite, latrobite, nephelin; in all, or the greater number of the clays (Mitscherlich, *Lehrb.* 2, 19); also in small quantity in limestones of the most various formations, in native oxide of manganese, specular iron ore, &c. (Kuhlmann, Wöhler & Beringer, *Ann. Pharm.* 41, 124 and 220); as chloride of potassium, sublimed from volcanos, and sparingly, in rock-salt; as sulphate, chloride, bromide, or iodide of potassium, in small quantities, in sea water, in the water of the Dead Sea, and in several salt-springs and other mineral waters (vid. Braylay and Cuff, *Phil. Mag. Ann.* 5, 411, 7, 9): in organic bodies, as carbonate, phosphate, sulphate, hydrochlorate, nitrate, and in union with organic acids.

*Preparation.*—1. Slightly moistened hydrate of potash is placed upon a platinum capsule attached to the negative pole of a voltaic battery containing from 100 to 200 pairs of plates, and touched by a platinum wire proceeding from the positive pole. The hydrate liquefies, and the globules of potassium, as they appear on the plate, are taken away and put into rock-oil before they can take fire. (H. Davy, I., 458.)

* In English, the terms *Potash* and *Potassa* are used almost indiscriminately; the latter is more uniform in termination with soda, lithia, baryta, &c.; but the former has the advantage in point of brevity and facility of pronunciation.—[W.]

2. A gun-barrel cleaned inside is bent upwards at the thick end at a very obtuse angle, and downward at the other end, for about four inches, the middle part being laid horizontally in the furnace. The middle part is covered with a luting composed of 1 part of clay, 5 parts of sand sifted through a hair sieve, and a small quantity of horse-dung; this luting is slowly dried and the cracks filled up with fresh material. The middle part of the gun-barrel is filled with 400 grammes or more of iron turnings, harpsichord wire, and iron filings (filings alone stop up the tube too much), and 120 grammes of pure hydrate of potash are put into the upper end. The lower end is connected airtight with a copper receiver, having a tube adapted to its opposite side to carry away uncondensed gases. The fire is raised by the bellows to a dull white heat, after which the upper end of the gun-barrel, which has meanwhile been kept cool by means of wet cloths, is allowed to get gradually warm. The hydrate then fuses, and is decomposed by the iron, and the hydrogen gas and potassium vapour thereby produced escape by the lower end of the gun-barrel. (*Sch.* 80.) The process generally yields about 80 grains of potassium. (Gay-Lussac & Thénard.) Berzelius heats the gun-barrel to redness, and passes hydrogen gas dried by chloride of calcium through it, in order to free it from oxide of iron before using it. The process often fails in consequence of the coating of clay breaking and falling off. For this reason, Mantell encloses the gun-barrel in a tube of baked clay, of such a width that the expansion of the gun-barrel by the heat may not burst it. The hydrate of potash may also, while the tube is in a state of ignition, be introduced by the upper opening, and the aperture immediately closed again; and a short glass tube-funnel (the neck of a broken retort) may be adapted to the lower end of the gun-barrel and made to dip a little below the surface of rock-oil contained in a glass receiver: with this arrangement, the progress of the operation may be watched by the escape of gas-bubbles, and the appearance of the drops of potassium. (Gm.) The method recommended by Tennant—which consists in heating to whiteness a mixture of hydrate of potash and iron filings in a short gun-barrel closed at the bottom, and having a narrow tube fitted to its upper end—appears less advantageous than the preceding.

3. *a.* A mixture of equal parts of carbonate of potash and charcoal moistened with a small quantity of oil—or burnt tartar only—is heated to whiteness in a short, coated gun-barrel, and the potassium, which rises in vapour, is received upon thick cold rods of iron, held about the twelfth of an inch above the mixture, and constantly changed: from these the drops of potassium are afterwards scraped with a knife under rock-oil. (Curaudau, *Sch.* 82.) The mass must not be pressed into the gun-barrel, or it will be thrown out by the gas which is produced. This process yields but a small quantity of potassium mixed with much carbonaceous matter.

*b.* According to the method of Brunner, improved by Wöhler, 6 pounds of crude tartar, previously ignited in a covered crucible and mixed with charcoal powder, are put into a wrought-iron quicksilver-bottle, to the mouth of which is screwed an iron tube not more than 5 inches long. The bottle is then placed in a powerful wind-furnace having a wide grate and a chimney 10 feet high, and made to rest on a stone at the back, while the tube passes through the wall of the furnace in front. The heat is raised till a gas, which takes fire spontaneously, and a greenish vapour, make their appearance; and the end of the tube is then connected with a receiver of iron or copper containing rock-oil, surrounded

with cold water which is frequently changed, and having a vent for the carbonic oxide evolved during the process.

In Liebig's laboratory, the furnace is so constructed that the bottle may be heated by flame instead of by direct contact with charcoal or coke. The mercury-bottle generally contains some globules of mercury, which must be expelled by previously heating the bottle and blowing out the vapour of mercury with a pair of bellows. Instead of a mercury-bottle, Kukla recommends one made for the purpose, of thick iron-plate. (*Zeitschr. Phys. v. W.* 5, 466.)—As these iron bottles gradually burn away and become perforated, and consequently do not last for more than one or two operations, it has been recommended to cover them with luting; but as the luting easily falls off and does not appear to afford much protection, Schädler and Werner (*J. pr. Chem.* 14, 267) surround the bottle with a wire-net: on this, the former applies a luting composed of 2 parts of pounded Hessian crucibles, 1 part of pipe-clay, and some cow-hair; the latter two or three coatings of a thin paste made of coarse quartz-sand and a little clay. Anthon (*Repert.* 58, 318) covers the bottle without any wire-net with a mixture of loam and sand; Gale (*Sill. Amer. J.* 19, 205; 21, 60) with a luting composed of equal parts of sand, clay, and soap-stone.

Werner mixes 20 oz. of charred tartar with 20 oz. of fine, and 3 oz. of coarse charcoal-powder (about the size of peas), and enough water just to moisten the mass. Instead of burnt tartar, a mixture of carbonate of potash and charcoal may be used; for example, 3lb. of pearl-ash dissolved in water, put into an iron vessel with 1½lb. of fine charcoal powder and stirred up with an iron spatula,—then 1½lb. of coarse charcoal added, and the whole dried completely. An excess of charcoal prevents—as Schädler has pointed out—the rapid choking of the tube connected with the mercury bottle with carbonaceous matter, as well as the fusion and projection of the contents of the bottle. Kukla evaporates to dryness a mixture of 3 parts of pearl-ash dissolved in water with 1 part of flour; carbonizes the residue; mixes it when cold with sufficient water to moisten it slightly; and puts it into the flask. The addition of iron filings is of no use, even when hydrate of potash is employed, because, at the temperature of the wind-furnace, the iron does not assist in the decomposition. (Brunner.)

The shorter and wider the iron tube which connects the bottle with the receiver, the less easily is it choked up. It must be either screwed or ground into the bottle: if the connexion is not perfect, the joint must be surrounded with clay. The bottle nearly touches the front wall of the furnace through which the tube passes. This wall is made either of thin tiles, a piece of a large black-lead crucible, or a plate of iron. The opening through which the tube passes is closed round with clay. Just outside the furnace, the tube has a square piece of iron with a hole in the centre, soldered on to it, so that it can be unscrewed from the bottle by means of a key. The neck of the receiver approaches very near this piece of iron, and receives about an inch of the tube, which is made to fit closely into it, and reaches just into the receiver itself.

The best form of receiver consists of two copper vessels, the lower of which is open at top and filled from one-third to one-half with rock-oil, while the upper, which is open below, passes loosely into the lower, and reaches to the bottom of it, so that the rock-oil forms the joint between them. The upper vessel has three openings on three of its sides towards the top. Through one of these holes the iron tube passes, and the one opposite to it is made a little smaller, and may be closed with

a cork. Through this, when the iron tube begins to be choked with carbonaceous matter, a hollow borer with a long wooden cross handle is passed and stirred about in the tube till a free passage is made. This must be done as often as a diminished escape of gas appears to indicate that a stoppage is forming. If a complete stoppage is actually formed, it becomes difficult, or even impossible to restore a passage; but even if the attempt is successful, masses of burning potassium may be forcibly thrown out by the sudden expansion of the compressed gas in the bottle, and occasion injury. To prevent accidents, the hands should be protected with gloves, and the operator should stand out of the way, so as not to be struck by the projected matter. The potassium adhering to the borer must be quickly scraped off into rock-oil kept in a small mortar, and covered over with a plate, if it takes fire.

Through the third opening of the upper part of the receiver the carbonic oxide escapes. This gas is accompanied by vapour of rock-oil, and likewise by a grey cloud of croconaceous matter, by which it is rendered very inflammable; and as it is still hot when it issues from the opening in the receiver, it takes fire, and burns slowly with a dull red light, often, however, bursting out into a strong bright flame. To prevent this combustion, and at the same time preserve the croconaceous matter, the gas is conducted from the third opening through a tin tube 3 feet long, into an iron bottle, where a great deal of croconaceous matter is deposited. After this the carbonic oxide escaping from the open bottle no longer takes fire, because it is much cooler and contains less croconaceous matter. It still, however, retains a peculiar smell, and excites coughing. Glass tubes and bottles must not be used, because the croconaceous matter deposited in them, after it has attracted a little moisture from the air, explodes violently—sometimes spontaneously, and sometimes while the vessels are being washed out with water, and breaks them to pieces.

The lower division of the receiver is immersed in an iron pan filled with cold water or ice: the ice or water is frequently renewed, but with great care, so that no water may get between the two parts of the receiver.

The rock-oil must be rectified and free from water: that which distils over during the latter part of the rectification is to be preferred, because it is less volatile.

With a low fire, the decomposition of the potash does not proceed satisfactorily; and if the fire be stronger than required, the mercury bottle is rapidly burned away. The supply of coals should be well kept up, otherwise the fire will get too low, and the subsequent addition of cold fuel will cool the bottle down and interrupt the operation. It takes from three to four hours to decompose the whole contents of the bottle. Frequently, however, the process is interrupted before this, either by a hole being burned in the mercury-bottle, or by the impossibility of removing the stoppage in the conducting-tube. In the latter case, the moveable grate is either lowered from beneath the mercury-bottle, or the bars are withdrawn, so that the evolution of gas may not go on and burst the bottle. Generally, however, the gas escapes through the worm by which the tube is screwed into the bottle.

As soon as the mixture is exhausted, or any accident occurs, the iron pan containing the water is taken from under the receiver, the two parts of which are then bound together with a cloth, and the upper one separated from the iron tube: a few light blows of a hammer are often necessary to accomplish this. The opening in the receiver is closed with a

stopper, and the whole left for a while to cool. The upper part of the receiver is then taken out from the under, and the matter adhering to both of them immediately moistened with rock-oil, that it may not inflame in the air; it is then scraped off and immersed in rock-oil. The rock-oil frequently takes fire during this operation: if so, it must be extinguished by covering the receiver with a piece of board or a cloth. By this mode of proceeding, all danger of explosion is avoided. If, on the contrary, the operator leaves the receiver loosely stopped for a considerable time—say over-night—the most dangerous explosions often occur on taking it asunder, masses of burning potassium being thrown about with great violence. This is not occasioned by the formation of an explosive gas (from admixture of atmospheric air with the hydrogen evolved in the decomposition of the moisture in the air by the potassium, or with vapour of rock-oil): an explosive mixture of this kind would not act so violently or scatter such quantities of matter about: moreover, the explosion frequently does not take place till after the receiver has been opened for some time and all the explosive gas must have escaped. The substance itself must, therefore, have become explosive from the slow entrance of moist air; and the increased rush of air which follows the opening of the vessel either causes inflammation and explosion at once; or that accident occurs during the scraping off of the contents of the receiver, especially if the mass has not been carefully saturated with rock-oil.

[For an account of these dangers, see especially Pleischl, *Zeitschr. Phys. v. W.* 3, 326.]

¶ Wöhler mentions an instance in which the croconaceous matter, after being kept in a sealed tube for ten days, and then turned out into a *dry* porcelain basin, immediately began to assume a purple-red tint, and in a few seconds exploded with a tremendous report, and broke the vessel to pieces. (*Ann. Pharm.* 49, 361.) ¶

The contents of the receiver consist of globules of potassium and a carbonaceous mass, which is a mixture of potassium and croconaceous matter. The globules of potassium must be picked out with a pair of forceps, washed with rock-oil from the black powder adhering to them, and preserved in a stoppered bottle under rock-oil. The black residue yields more potassium by distillation (*vid. seq.*); or, if it contains but little of the metal, rhodizonate or croconate of potash may be separated from it by digesting it in water. (Vid. *Rhodizonic* and *Croconic Acids.*)

From the iron tube also, which should be unscrewed as soon as possible from the bottle, after it has been taken out of the fire, more impure potassium may be scraped after it has been cooled, and the contents soaked in rock-oil. Pleischl obtained from 36 oz. of carbonized tartar (produced from 6 lb. of tartar) mixed with 6 oz. of charcoal, 9¼ oz. of potassium, or 9·2 per cent. From 96 lbs. to 120 lbs. of coals were burned during the operation. 100 parts of tartar contain 21 parts of potassium, so that about one-half is obtained. Much more than this can hardly be expected, considering the many sources of loss from perforation, the formation of croconaceous matter, &c., &c. In most cases the product is much less.

*Purification.* The potassium obtained by the third method is mechanically, or, according to some, chemically combined with carbonaceous matter. The croconaceous matter united with the potassium imparts a reddish-yellow colour to the solution when the potassium is put into water.

*Purification by Filtration.* The impure potas[illegible] up in a linen bag heated to 60° or 65° (140° or 149° F.), [illegible] with a

pair of wooden tongs. (The black residue still contains potassium, which may be recovered by distillation.) The potassium thus pressed out, is as free from carbon as that which is purified by distillation, but the loss by oxidation is greater. (Pleischl.)

*Purification by distillation.*—By this method not only may the purer portion of the potassium be obtained quite free from carbon, but likewise the carbonaceous mass may be made to yield a considerable quantity of the metal. Iron vessels are better adapted for the distillation than glass vessels. Into the wide neck of a wrought or cast-iron bottle, a short, bent, pistol-barrel is inserted: the bottle is filled with the potassium or carbonaceous matter, and very slowly raised to a strong red heat in a small air-furnace, the tube having been previously adjusted in an inclined position. The rock-oil adhering to the potassium passes over first into the glass vessel prepared to receive it, and then the potassium follows. Part of the metal condenses in the tube, so that towards the end of the distillation the greater part of the tube must likewise be surrounded with fire. To prevent the rock-oil from taking fire in the receiver, the short neck of a broken retort should be adapted by means of asbestos to the end of the pistol-barrel, and passed into the receiver, which it should closely fit, so as to dip just below the surface of the rock-oil. Even when the black mass has been subjected to distillation in this manner, it may still give rise to dangerous explosions on being exposed to the air and scraped, after cooling.

The potassium is preserved under rock-oil in very close vessels capable of holding but a small quantity of air, or in hermetically sealed glass tubes.

*Properties.* Silver-white, with a strong lustre; specific gravity = 0·86507. (Gay-Lussac & Thénard.) Crystallizes by sublimation in cubes; its cut surface also shows cubical markings (Pleischl, *Zeitschr. Phys. v. W.* 3, 1): when broken, it exhibits small, shining, crystallized faces. (Sir H. Davy).—At 0° it is brittle; at 19° (66·2° Fah.) soft as wax; begins to melt at 25° (136·4° Fah.).—Sublimes in green vapours, at a temperature below redness. It is a very good conductor of heat and a perfect conductor of electricity. (H. Davy.)

Atomic weight of potassium; 39·144. (Pelouze, *Compt. rend.* 20, 147); 39 (Maumené. *N. Ann. Chim. Phys.* 18, 41.)

## *Compounds of Potassium.*

### Potassium and Oxygen.

### A. Suboxide of Potassium.

This compound is formed: 1. When potassium in thin laminæ is left in contact with a small quantity of air in a close vessel.—2. When protoxide or peroxide of potassium is heated with potassium.—Forms a bluish-grey brittle mass without metallic lustre, exceeding potassium in specific gravity. Very fusible. Takes fire in the air often at 20° or 25° (68°—77° Fah.), and becomes peroxidized; decomposes water, without however taking fire. (H. Davy, Gay-Lussac & Thénard.) Probably, a mere mixture of potassium and potash.

## B. Potash. KO.

*Potassa, Protoxide of Potassium, Vegetable Alkali, Pflanzenlaugensalz, Fixed Vegetable Alkali, Kali, Potasse, Oxyde de Potassium.*

*Formation.* Potassium in contact with moist air or oxygen gas at ordinary temperatures, gradually decomposes a portion of the water, and is converted into hydrate of potash. In cold dry air it remains unchanged. (Bonsdorff.) The metal decomposes water with great evolution of heat, which, when oxygen gas is present, sets fire to the hydrogen evolved, and likewise to the potassium itself. If potassium be introduced into a vessel filled with water and standing over mercury, a solution of potash is obtained, heat being generated and hydrogen gas rapidly evolved. Potassium thrown on water burns with a white, red, and violet flame: the little glowing ball of peroxide which remains finally dissolves in the water, with explosion. The same combustion occurs upon ice. If the burning globules of potassium, as they swim about on the water, are struck with a spatula, an explosion follows. (Couerbe.)—If a small piece of potassium be thrown upon a surface moistened with water in such a manner that it may rebound from thence to a dry place, it will continue to burn. The potassium, therefore, at first evolves hydrogen gas, which, together with the potassium, is set on fire by the heat produced: the further production of flame is due principally to the combustion of the potassium. Dilute acids behave in the same manner as pure water, but their affinity for potash induces a more rapid oxidation of the potassium. [For the motions of potassium on mercury, *vid.* Vol. I. p. 337.]—2. Potassium—either at ordinary temperatures or at a heat not above redness—decomposes carbonic oxide, carbonic acid (*Scheme* 21), boracic, phosphoric, sulphurous, and sulphuric acid—nitrous and nitric oxide gas—nitrous and nitric acid, (if the nitric acid be concentrated, a very dangerous explosion ensues *Kuhlmann*), arsenious, arsenic, molybdic, tungstic, and chromic acids; also the oxides of titanium, chromium, uranium, manganese, cobalt, tellurium, bismuth, and zinc; the three oxides of antimony, the two oxides of tin, the three oxides of lead, the two oxides of iron, the two oxides of copper, and the two oxides of mercury; also the oxides of nickel, silver, and platinum. In most cases, a complete reduction of the heavy metal takes place. Oxide of lead contained in a glass tube is likewise reduced by heated potassium.—Lastly, potassium decomposes, with the aid of heat, all carbonates, phosphates, sulphites, sulphates, nitrates, arsenites, and arseniates (but not the borates): in this action, it withdraws the oxygen, not only from the acid, but also from the base, when the latter is the oxide of a heavy metal.—Most of the above decompositions are attended with development of light and heat; and the product is generally potash, partly pure, and partly mixed with a portion of the original undecomposed oxide. (H. Davy, Gay-Lussac & Thénard.)

*Preparation.* 39 parts (one atom) of potassium are added to 9 parts (one atom) of water, in a vessel from which air is excluded; or 39 parts (one atom) of potassium are heated with 56 parts (one atom) of hydrate of potash.—2. By exposing peroxide of potassium to a strong heat. (H. Davy.)

*Properties.* Grey, solid substance, without metallic lustre, brittle, and having a conchoidal fracture; harder and apparently also heavier than the hydrate of potash. It melts a little above a red heat, but volatilizes only at a very high temperature. (H. Davy.) Specific gravity about = 2·656 (Karsten). Inodorous; highly caustic to the taste, and, when combined with water, the most destructive of all alkalis in its action on organic substances. In solution, it restores the blue colour of tincture of litmus reddened by acids, and turns an infusion of logwood red, an infusion of violets or red cabbage, green, and an infusion of turmeric, reddish-brown. The limits of these reactions on paper coloured with the different infusions are found at the following degrees of dilution. Red cabbage: one part of anhydrous potash dissolved in 9000 parts of water: Logwood; one pt. in 24,000 pts. of water: Turmeric; one pt. in 36,000 pts. of water; and red litmus paper; one pt. in 75,000 pts. of water. (Harting, *Journ. pr. Chem.* 22, 49.)—A solution of potash, not too dilute, gives a precipitate with the following substances. *Perchloric Acid:* a crystalline precipitate of perchlorate of potash. *Hydrofluosilicic Acid* in excess: a transparent, gelatinous precipitate of double fluoride of silicium and potassium: this precipitate is not very distinct, but becomes cloudy and more visible on the addition of ammonia. Concentrated solution of *Sulphate of Alumina* in excess produces, after the addition of an acid, a crystalline precipitate of octohedral alum. Solution of *Bichloride of Platinum:* pale yellow, and finely divided, or—when it comes out more slowly—orange-coloured, crystalline precipitate of double chloride of platinum and potassium.—Concentrated solution of *Tartaric Acid* in excess: crystalline precipitate of bi-tartrate of potash.—*Carbazotic Acid:* yellow needles of carbazotate of potash. If the solution of potash is much diluted, the precipitates appear only after a considerable time—and not at all, when the dilution is carried to a still greater extent.

| | Calculation. | | Berzelius. | Sir H. Davy. | Gay-Lussac & Thénard. |
|---|---|---|---|---|---|
| K | 39·2 | 83·05 | 83·0484 | 85 | 83·371 |
| O | 8·0 | 16·95 | 16·9516 | 15 | 16·629 |
| KO | 47·2 | 100·00 | 100·0000 | 100 | 100·000 |

(KO = 489·92 + 100 = 589·92. Berzelius.)

*Decomposition.*—1. By electricity.—2. By iron or zinc at a white heat.—3. By charcoal at a white heat.—4. At a red heat, by chlorine, into chloride of potassium and oxygen (*Sch.* 8):—by sulphur, into sulphide of potassium and sulphate of potash:—by phosphorus, into phosphide of potassium and phosphate of potash.

*Combinations. a.* With water.

*a.* Hydrate of Potash. *Caustic, Lapis causticus.*

Formed by exposing potassium to moist air.—One atom of anhydrous potash mixed with one atom of water, evolves sufficient heat to fuse the hydrate which is produced, and raise it to redness. (Berzelius.)

*Preparation.* 1. From carbonate of potash. In an iron vessel provided with a closely fitting cover, one part of carbonate of potash is heated with 12 parts of water till it boils; and slaked lime—made by mixing ¾ pts. of burned lime with 3 parts of warm water, and keeping it in a covered pan till the lime is reduced to a soft powder—is then added by degrees. After each addition of slaked lime, the mixture is boiled for a few minutes, in order that the carbonate of lime may become

dense, and fall down readily to the bottom. When all the lime has been added, the whole is boiled for a quarter of an hour, with the cover on, and left for the lime, &c. to settle down. The caustic solution—which should no longer effervesce, when poured into hydrochloric acid, or give any, or very little cloudiness with lime water, (if otherwise, longer boiling, and perhaps, also, an addition of milk of lime is requisite) is then drawn off into stoppered bottles, by a syphon first filled with water. The residue is once or twice boiled for half an hour with a small quantity of water, and the remaining portion of potash separated by subsidence and decantation. The rest of the lime is deposited in the stoppered bottles. The decanted solution is first rapidly concentrated in covered iron pots; and if it becomes turbid, set aside in stoppered vessels, and then decanted; and lastly, rapidly boiled down in a silver basin, till the oily hydrate which remains begins to evaporate as a whole in white clouds. (*Vid.* Mohr, *Ann. Pharm.* 23, 338.)

If the lime which is put into the solution of carbonate of potash is not slaked but merely pounded, it does not diffuse itself properly through the liquid, and the greater part is rendered useless, so that a much larger quantity is required to withdraw the carbonic acid, and the separation of the alkali from the calcareous precipitate is thereby rendered much more difficult. To ensure the complete separation of the carbonic acid from the potash, it is necessary to use a considerable quantity of water. When only 4 parts of water are used to 1 part of carbonate of potash, no decomposition takes place; and a concentrated solution of caustic potash withdraws the acid from carbonate of lime. (Liebig, I., 124.) When one part of carbonate of potash dissolved in 4 parts of water is boiled with hydrate of lime, it gives up only $\frac{3}{4}$ of its carbonic acid; with 5 parts of water, $\frac{2}{3}\frac{0}{1}$; and with 8 parts, almost the whole. (Watson, *Phil. Mag. J.* 3, 314.) Even with 10 parts of water to 1 part of carbonate of potash, the carbonic acid is not entirely separated; but with 50 parts of water the separation is complete. (Mitscherlich, *Lehrb.* 2, 15.) The lime may also be mixed with the solution of carbonate of potash at ordinary temperatures, and the liquid set aside in stoppered vessels; but then the decomposition proceeds more slowly, and frequent shaking is required; moreover, the carbonate of lime is less dense than when the liquid is boiled, and consequently the decantation is more difficult. It is to be observed also that carbonate of potash almost always contains silica, which is not precipitated at ordinary temperatures, but completely by sufficient boiling; for it then forms an insoluble compound with the excess of lime and the potash. Any alumina which may perchance be present is separated in the same way. (*Vid.* Bucholz, *Taschenb.* 1812, 156; Dobereiner, *Schw.* 10, 113.) It is better to decant the solution than to filter it through a cone of bleached linen; because the alkali extracts certain matters from the linen which colour the liquid yellow, and also because in filtering, it is less easy to guard against access of air. As the alkaline solution absorbs carbonic acid from the atmosphere very greedily, the air must be kept from it as much as possible. A portion of carbonic acid is always reabsorbed during evaporation, unless this process is performed in a silver vessel fitted with a head. When the caustic solution is evaporated down to an oily consistence, the greater part of the carbonate separates in solid particles, which swim on the surface, and can then be taken off by means of a spatula. If crude potash or pearlash is used instead of pure carbonate of potash, the hydrate of potash produced contains the chloride of potassium and sulphate of potash present in the original substance. Hence, to obtain hydrate of

potash in a pure state, it is necessary to make use of pure carbonate of potash. According to Berthollet's plan, however, tolerably pure hydrate of potash—the *Potasse à l'alcool*—may be obtained from impure carbonate. (*Crell. Ann.* 1786, 2, 211.) The caustic solution, obtained as above, is evaporated to the thickness of syrup, shaken in close vessels with $\frac{1}{3}$ of its volume of alcohol, and the mixture left to settle. Two strata are formed: the lower stratum is an aqueous solution of chloride of potassium, carbonate and sulphate of potash, together with a portion of caustic potash, and rests on a precipitate which may contain lime, oxide of iron, and sulphate of potash; the upper stratum is a solution of caustic potash with some chloride of potassium in alcohol. This is poured off, and freed from the greater part of the spirit, by distillation in a silver vessel furnished with a still-head, and boiled down in a silver basin till the hydrate begins to sublime. The resinous matter produced by the decomposition of the alcohol, and found swimming on the surface, is then removed and the hydrate poured out on plates. It is free from sulphate of potash, but contains chloride of potassium, and traces of carbonate and acetate of potash.

2. From sulphate of potash.—Powdered crystals of sulphate of potash are dissolved in a concentrated solution of baryta till a small portion of the liquid taken for trial gives a precipitate with chloride of barium, to which hydrochloric acid has been added in large excess —a proof that some sulphate of potash still remains undecomposed. Baryta-water is then carefully added in sufficient quantity just to decompose the sulphate, or still better, slightly in excess. The decanted solution is then evaporated, during which process the small excess of baryta is precipitated by the carbonic acid in the air. (Schubert, *J. pr. Chem.* 26, 117.) This method is more expensive, but yields—provided the baryta-water is good—a pure preparation, since sulphate of potash is more readily obtained in a state of perfect purity than the carbonate.

Hydrate of potash is preserved in air-tight glass bottles.

*Impurities. Carbonate of lime,* originating from imperfect decantation; *Oxide of Iron,* when the caustic solution is evaporated in an iron vessel to such an extent, that it begins to act upon the iron. These, together with other insoluble substances accidentally present, remain behind when the potash is dissolved in water. *Peroxide of Potassium:* Formed in small quantity, towards the end of the evaporation when conducted in the air. It is owing to the presence of this substance, that the hydrate of potash, when dissolved in water, gives off oxygen gas. The *lapis causticus* of the surgeon, which is prepared by evaporation in iron vessels, evolves a considerable quantity of oxygen, the amount of which appears to be in direct ratio with that of the oxide of iron, which is separated when the potash is dissolved in water. (Graham, *Edinb. J. of Sc.* 7, 187; J. Davy, *N. Edinb. Phil. J.* 6, 132.) [This connexion with the oxide of iron suggests the supposition that ferrate of iron is formed.] *Carbonate of Potash:* The solution effervesces with acids.—*Sulphate of Potash:* Chloride of barium, with excess of dilute hydrochloric acid, gives a precipitate. *Chloride of Potassium:* A precipitate produced even when the liquid is very dilute, with a solution of silver, nitric acid being added in excess.—*Nitrate of Potash:* Gives the reactions of the nitrates. (II., 401.)—*Certain oxides of the heavy metals:* The solution, supersaturated with acetic acid, gives a precipitate with sulphuretted hydrogen or sulphide of ammonium.

*α.* Hydrate of potash is a white, hard, brittle substance, having a specific gravity of 2·1 (Dalton), and often a fibrous texture. It melts below redness, forming an oily liquid, clear as water, which volatilizes at a full red heat in white pungent vapours. Hydrate of potash heated on platinum-wire, colours the blowpipe flame violet. (Fuchs.)

| | Calculation. | | H. Davy. | Gay-Lussac & Thénard. | Berthollet. | Darcet. |
|---|---|---|---|---|---|---|
| KO..... | 47·2 | 84 | 83 to 82 | 81·55 to 79·28 | 86·36 | 73 to 72 |
| HO..... | 9·0 | 16 | 17 — 18 | 18·45 — 20·72 | 13·64 | 27 — 28 |
| | 56·2 | 100 | 100 — 100 | 100·00 — 100·00 | 100·00 | 100 — 100 |

The amount of water present in hydrate of potash is best found from the loss of weight which it sustains when heated to redness with a known quantity of vitrefied boracic or silicic acid. By ignition in contact with charcoal it is converted—according to Bussy (*J. Pharm.* 8, 266) with evolution of carburetted hydrogen (?)—into carbonate of potash.

*β.* Crystallized Potash. *Caustic Salt.*—Crystallizes on cooling from a concentrated solution of caustic potash. (Löwitz, *Crell. Ann.* 1796, 1, 306.) Transparent, colourless, very acute rhombohedrons with truncated terminal edges. When placed in vacuo over oil of vitriol, it effloresces to an opaque mass, consisting of 78·6 parts of potash and 21·4 parts of water. (Ph. Walter, *Pogg.* 39, 192.)

| | Calculation. | | Walter. |
|---|---|---|---|
| KO..... | 47·2 | 51·19 | 49·9 |
| 5HO .... | 45· | 48·81 | 50·1 |
| | 92·2 | 100·00 | 100·0 |

*γ.* Aqueous Solution of Potash. *Caustic-solution, Soapboilers'-ley, Seifensieder-lauge,* and at a certain degree of concentration, *Meister-lauge.*—Potash, hydrate of potash, and crystallized potash deliquesce rapidly in the air; the first two dissolve in water with considerable rise of temperature; the crystals produce great cold. Hydrate of potash requires but half its weight of cold water to dissolve it. (Löwitz.)—Preparation. (III., 11—13.) The solution is kept in bottles with glass or cork stoppers. In either case, none of the solution should touch the stoppers; for those of glass become in a short time so strongly cemented in, that they cannot again be withdrawn; and corks corrode and impart a brown colour to the liquid. When bottles made of white glass are used to contain the solution, they frequently crack in all directions. After being long kept, the liquid often deposits brownish-white flakes. These were found by the author to consist of silica, with small quantities of alumina, lime, potash, oxide of iron, and a trace of oxide of copper (Gmelin), and are probably produced by the action of the potash on the glass.

Colourless liquid, having, when highly concentrated, an oily consistence and considerable density. A solution made with equal parts of hydrate of potash and water does not freeze at −54° (−65° F.). (Guyton-Morveau.) One measure of solution of potash of 22° Bm. mixed with one measure of water undergoes a condensation amounting to 0·045 of the volume of the water: and all the air present in the water is expelled. (Payen, *Ann. Chim. Phys.* 50, 305.)

*Quantity of Anhydrous Potash contained in Solutions of Potash of various densities.*

| (Dalton, *System.* 2, 293.) | | | (Tünnermann, *N. Tr.* 18, 2, 5); at 15°. | | | |
|---|---|---|---|---|---|---|
| Sp. gr. | Potash per cent. | Boiling point. | Sp. gr. | Potash per cent. | Sp. gr. | Potash per cent. |
| 2·40 | 39·9 | 129·5° | 1·3300 | 28·290 | 1·1437 | 14·145 |
| | | | 1·3131 | 27·158 | 1·1308 | 13·013 |
| 2·20 | 36·8 | 123·9 | 1·2966 | 26·027 | 1·1182 | 11·882 |
| 1·42 | 34·4 | 118·3 | 1·2805 | 24·895 | 1·1059 | 10·750 |
| 1·39 | 32·4 | 115·5 | 1·2648 | 23·764 | 1·0938 | 9·619 |
| 1·36 | 29·4 | 112·2 | 1·2493 | 22·632 | 1·0819 | 8·487 |
| 1·33 | 26·3 | 109·4 | 1·2342 | 21·500 | 1·0703 | 7·355 |
| 1·28 | 23·4 | 106·6 | 1·2268 | 20·935 | 1·0589 | 6·224 |
| 1·23 | 19·5 | 104·4 | 1·2122 | 19·803 | 1·0478 | 5·002 |
| 1·19 | 16·2 | 103·3 | 1·1979 | 18·671 | 1·0369 | 3·961 |
| 1·15 | 13·0 | 101·7 | 1·1839 | 17·540 | 1·0260 | 2·829 |
| 1·11 | 9·5 | 101·1 | 1·1702 | 16·408 | 1·0153 | 1·697 |
| 1·06 | 4·7 | 100·5 | 1·1568 | 15·277 | 1·0050 | 0·5658 |

*b.* With acids potash forms the POTASH-SALTS. Of all bases, it possesses the strongest affinity for the greater number of acids, and next to ammonia neutralizes them most completely, so that in salts formed with the weaker acids, the alkaline reaction of the base predominates. The potash-salts are colourless when the acid itself is so. They are fixed in the fire, unless the acid in combination with the potash has very little affinity for it or is readily decomposed. Salts of potash impart a violet colour to the blowpipe flame on platinum wire. (Fuchs.) Alcohol heated with a salt of potash in powder and then set on fire burns with a blue or violet flame. (H. Rose.) The salts give a blue colour to a bead of borax in which pure oxide of nickel is dissolved. (Harkort, *Pogg.* 9, 182.) They yield no precipitate when melted with carbonate of soda on platinum foil. (Berzelius.) All potash-salts are soluble in water, and for the most part readily so. The solution of a salt of potash, when very dilute, gives a precipitate with other liquids only when the acid combined with the potash forms an insoluble compound with the substance added or with a portion of it—or when the acid is itself set free, and is insoluble in that state. A concentrated solution, on the contrary, exhibits the same reactions as a solution of potash (p. 11), namely, with perchloric acid, tartaric acid, carbazotic acid, sulphate of alumina, hydrofluosilicic acid, and chloride of platinum, the reagents being used in the concentrated state. In the case of tartaric acid, an excess of sulphuric, hydrochloric, or nitric acid interferes with the appearance of the precipitate. Those salts of potash, which would throw down the alumina from alum (for instance, the carbonate), must be previously mixed with sulphuric acid. If nitrate of potash is dissolved in so much water that 205 parts of water contain only 1 part of potash, chloride of platinum will still produce a precipitate; with 210 parts of water this effect no longer takes place. Again; tartaric acid acts with 220 parts of water to 1 part of potash, but not with 230 parts. (Harting, *J. pr. Chem.* 22, 49.) With solution of sulphate of potash, the limits of reaction are 1 part of potash in 200 parts of water for chloride of platinum, and 400 parts of water for tartaric acid. (Lassaigne, *J. Chim. Med.* 8, 527.)

Potash forms *double salts* with ammonia, soda, magnesia, the protoxide and sesqui-oxide of cerium, yttria, alumina, thorina, zirconia, the sesqui-oxides of chromium and uranium, the protoxide and sesqui-oxide of

manganese, sesqui-oxide of antimony, the oxides of zinc, and cadmium, the protoxide and sesqui-oxide of iron, protoxide of cobalt, oxide of nickel, the di-oxide and protoxide of copper, protoxide of mercury, oxide of silver, teroxide of gold, the protoxide and bi-oxide of platinum, bi-oxide of palladium, sesqui-oxide of rhodium and sesqui-oxide of iridium.

*c.* Potash combines with the earths, forming vitreous and other compounds, and also various minerals.

*d.* With many oxides of the heavy metals, not having an acid character, sometimes in the dry, sometimes in the wet way, namely, with the oxides of zinc, tin, lead and gold.

*e.* With several organic-bodies not possessed of acid properties; for instance, with alcohol.

### C. Peroxide of Potassium. $KO^3$.

Discovered by Gay-Lussac & Thénard.—*Formation and Preparation.* 1. Potassium takes fire in air or oxygen-gas at temperatures between 60° and 80° (provided the metallic surface is renewed), and burns with a dazzling white or red flame, producing peroxide of potassium. Platinum or silver-foil, covered with fused chloride of potassium, may be used as a support.—2. Peroxide of potassium is likewise formed by the combustion of the suboxide, or when anhydrous potash or hydrate of potash (or the hydrate mixed with potassium: *H. Davy*) is heated to redness for a long time in dry oxygen-gas.—3. Impure peroxide of potassium may be obtained by gently heating potassium in nitrous or nitric oxide gas or with nitre or certain metallic oxides; also by the ignition of nitre. (Gay-Lussac & Thénard.)

*Properties.* Orange-yellow. Fuses somewhat less easily than hydrate of potash to a brown transparent oil, and crystallizes in scales on cooling. (Gay-Lussac & Thénard.)

| | Calculation. | | Gay-Lussac & Thénard. | |
|---|---|---|---|---|
| K | 39·2 | 62·03 | 65 | |
| 3O | 24·0 | 37·97 | 35 | |
| $KO^3$ | 63·2 | 100·00 | 100 | |

*Decompositions.* 1. By a white heat, into potash and oxygen. (H. Davy.)—2. By water at ordinary temperatures, with effervescence, and production of heat, into oxygen and solution of potash; by carbonic acid or hydrochloric acid gas aided by heat, into oxygen and carbonate of potash, or oxygen, water, and chloride of potassium.—3. By combustible bodies.—Heated in hydrogen gas it is converted, without incandescence, into hydrate of potash and water. Ignited with charcoal it yields carbonate of potash, the change being accompanied by vivid combustion. It acts in a similar manner on resin, wood, or albumen. With phosphorus it forms phosphate of potash, the action being attended with the most vivid combustion; with sulphur, it forms sulphate of potash and a small quantity of sulphide of potassium, the combustion in this case being less vivid. Heated in sulphurous acid gas, it inflames and yields sulphate of potash and oxygen gas. When it is heated in phosphuretted or sulphuretted hydrogen gas, phosphide, or sulphide of potassium is formed, accompanied by flame; heated in nitrous gas, it forms nitrite of potash and hyponitric acid vapour. By heating it in ammoniacal gas, hydrate

of potash and nitrogen gas are obtained without any evolution of light and heat. It oxidizes potassium, arsenic, antimony, tin, zinc, and copper with incandescence, and bismuth, lead, and iron, and even silver and platinum without incandescence. (Gay-Lussac & Thénard.)

## Potassium and Hydrogen.

### *Hydride of Potassium?*

Potassium heated not quite to redness in pure hydrogen gas absorbs about $\frac{1}{4}$ as much of this gas as it would have evolved by contact with water, and is converted into a grey powder, without metallic lustre, and infusible below a red-heat. At a red heat it is resolved into potassium and hydrogen gas; and by mercury, especially if hot, it is converted into hydrogen gas and an amalgam of potassium. It inflames spontaneously in the air. With water it evolves about $\frac{5}{4}$ as much hydrogen as the potassium contained in it would have set free; it likewise takes fire on water. (Gay-Lussac & Thénard.) Sir H. Davy denies the existence of this body.—Jacquelain (*Ann. Chim. Phys.* 74, 203,) confirms its existence, and founds upon this absorption of hydrogen by potassium, a method of separating hydrogen from marsh gas and olefiant gas.

When potassium is heated in hydrogen gas, the hydrogen acquires the property of inflaming in the air and burning with a brilliant flame and formation of alkaline fumes; but as it cools, it deposits the potassium and loses its power of spontaneous combustion. (H. Davy.)—In the preparation of potassium from hydrate of potash and iron-filings, a colourless gas is produced which is heavier than hydrogen, takes fire in the air at ordinary temperatures, and burns with a pale yellow flame, forming water and potash;—if left to itself for a few hours, or placed in contact with water, it loses a portion of its potassium, and with it, the power of taking fire at ordinary temperatures, even though it still retains a portion of the potassium. (Sementini.) This gas, Sementini regards as potassuretted hydrogen gas; it is however considered by Berzelius and Brunner as hydrogen gas in which the vapour of potassium is simply diffused, so that it is again deposited on cooling.

## Potassium and Carbon.

### A. *Carbide of Potassium?*

Charcoal, exposed to a red heat in contact with potassium,—at which temperature the potassium if alone must have been volatilized,—effervesces afterwards with water. (H. Davy.) Perhaps several of those carbonaceous substances, which inflame spontaneously in the air (pyrophoric charcoals, as they are called) are carbides of potassium.—The black mass also, which passes over in the preparation of potassium by Curaudau's or Brunner's method, is regarded by Berzelius as a carbide of potassium. [Probably, for the most part, belonging to the croconaceous matter.]

## B. Carbonate of Potash.

*α.* Simple Carbonate.—*Basic, unsaturated Carbonate of Potash,* (Berthollet) *Mild, aerated Vegetable Alkali, Salts of Tartar, Purified Potash, Pearlash; Alkali vegetabile fixum, Sal tartari, Cineres clavellati depurati.*

*Preparation.*—1. *Crude Potash.* From the ashes of inland-plants, consisting chiefly of carbonate, sulphate, and silicate of potash, chloride of potassium, carbonate and phosphate of lime, magnesia, alumina, silica and the oxides of iron of manganese. The ashes are soaked in tubs of water, which chiefly dissolves the four first mentioned substances (amounting to between 5 and 32 per cent. of the ash). The alkaline solution is then boiled down in iron pans to such a degree of concentration that it solidifies to a brown mass on cooling. The brown colour proceeds from organic matter extracted from the woody fibre still present in the ash, from the wood of the tubs, and from the straw which is put round the cocks used in drawing the ley from the tubs. The crude potash thus obtained is heated to redness on the level hearth of a reverberatory furnace, over which the flame plays, and constantly stirred about with an iron rod till all the water is drawn off, and the organic matter consumed: *Burnt* or *calcined Potash, Cineres clavellati.* This substance contains, besides carbonate of potash, several impurities, some of which are insoluble in water: viz., ashes, charcoal, small stones from the furnace, &c.; and some soluble in water: viz., a large quantity of chloride of potassium, sulphate and silicate of potash, traces of manganate of potash (which imparts a blue colour to the mass) and phosphate of potash (Kobell, *Kastn. Arch.* 8, 322), carbonate of soda (Berthier), and oxide of copper. (Sarzeau, *J. Pharm.* 18, 656.) A particular specimen of crude potash, from Kasan, obtained from wood-ashes, contained in 100 pts. (1) insoluble in water: Lime 0·054, alumina 0·012, oxide of manganese 0·013, silica 0·122; (2) soluble in water: Potassa 47·455, combined with carbonic acid 25·890, and silica 0·344; sulphate of potash 17·062; phosphate of potash 0·443; chloride of potassium, 3·965; and carbonate of soda 4·630. In this specimen of potash, 9 atoms of carbonic-acid were combined with 8 atoms of potassa. (R. Hermann, *J. Pr. Chem.* 22, 442.)—Preuss (*Ann. Pharm.* 34, 239) thought that he had discovered iodine in a sample of potash.

2. *Purified Potash, Pearlash, Cineres clavellati depurati.* Crude potash is dissolved in 2 parts of boiling water, and the solution after being filtered through white blotting-paper or bleached linen, is evaporated in an iron pot to the proper degree of concentration: it is then left at rest for a day till all the sulphate of potash has crystallized out, and poured off from the crystals. If it renders solution of chloride of barium turbid after being supersaturated with hydrochloric acid, a second evaporation and cooling is necessary to get rid of the remaining sulphate of potash. The clear solution is boiled down (to the density of about 1·43) till it is covered with a crystalline film, which can no longer be removed by stirring the boiling liquid, and then cooled, stirring all the while, whereupon most of the carbonate of potash crystallizes out. The mother-liquid is drained off by filtration, and is found to contain a large quantity of carbonate of *potash, together* with certain impurities, chiefly consisting of chloride of *potassium and silicate* of potash. The crystals of carbonate are lastly

washed with a small quantity of cold water and then rendered anhydrous by heating them to incipient redness in vessels of cast-iron, silver, or platinum. Some chloride of potassium and silicate of potash still remain; the silica may be separated by means of charcoal (see below), but the chloride of potassium cannot be entirely removed.

To treat 1 part of crude potash with only 0·6 of cold water, and then strain and evaporate after prolonged agitation, is less economical, because a large quantity of the carbonate of potash always remains in the residue. It is said that by this method, the solution of the sulphate of potash is avoided; some of that salt is, however, liable to be dissolved in consequence of the heat developed on mixing the potash with the water. The best way of getting rid of the sulphate is by evaporating and cooling the solution obtained as above by the aid of heat. If the solution thus freed wholly or in part from sulphate of potash is evaporated without further precaution, as is generally the practice, all the chloride of potassium and silicate of potash remain mixed with the carbonate. The method just given of separating the greater part of the two salts by crystallizing the carbonate, is due to Mayer. (*Pogg.* 46, 651.) In order to free the carbonate of potash from all the silica, a solution of 1 part of carbonate in 1 part of water, is mixed with $\frac{1}{4}$ part of powdered charcoal, the mixture left for 24 hours and frequently agitated, and then filtered. (Artus, *J. pr. Chem.* 15, 124.) The manganate of potash present is almost always decomposed by the deoxidizing action of the substance of the filter, but the purified potash when heated to redness often assumes a bluish tint from the presence of a trace of this salt, introduced possibly with some ash which may have fallen in.

3. *Salt of Tartar, Sal Tartari.* Purified tartar is heated to low redness in a covered crucible made of iron, silver, or platinum; the carbonaceous residue put into a boiler of iron, silver, or platinum, and the carbonate of potash extracted by hot water. The filtrate is then allowed to stand for some days in a vessel of glass or procelain, to allow the carbonate of lime to subside; filtered again, and evaporated to dryness in an iron, silver, or platinum pan. The residue is covered with 3 parts of cold water, and the solution, after 3 days, decanted from the insoluble matter and evaporated to dryness. The salt of tartar thus obtained contains, according to Wackenroder (*Ann. Pharm.* 24, 17), mere traces of chlorine, lime, magnesia, and silica; Kobell asserts that some phosphate of potash is also present. If crude tartar is used for this purpose, a large quantity of cyanide of potassium is formed (from the ferment which it contains), and remains mixed with carbonate of potash. Even the purified tartar of commerce requires to be re-purified before it is used. For this purpose, it is either dissolved in boiling water and allowed to crystallize from the filtrate, or washed several times on a linen cloth with cold water. (Wackenroder.) Or, after being finely pounded, it is boiled for an hour in a glass vessel, with an equal quantity of water and $\frac{1}{16}$ of hydrochloric acid; the solution containing lime is poured off when cold; and the tartar washed on a filter with water, till that which passes through no longer gives a precipitate with a solution of oxalate of potash or a salt of silver. (Stürenberg and Dulk, *N. Br. Arch.* 20, 60.) If the tartar be decomposed by putting it into a paper cone and heating it in the open fire, impurities and loss can scarcely be avoided. If an earthen crucible is made use of, the potash unites with a portion of the silica contained in it. This may be avoided, according to Wackenroder, by lining the crucible with a mixture of starch and gum.

4. *Black Flux, Fluxus niger.* A mixture of carbonate of potash and charcoal, obtained by detonating a mixture of 2 parts of tartar and 1 part of nitre. The carbonate of potash may be extracted by water. If the mixture be thrown, by small portions at a time, into a red-hot iron crucible, the residue obtained is free from nitrate of potash, but contains cyanide of potassium; the latter is also present, though in smaller quantity, even when purified tartar is used. If the mixture is put into an iron dish and set on fire by a red-hot wire, the decomposition is incomplete, unless the dish is heated to redness afterwards; the mass is also found to contain nitrite of potash, but no cyanide of potassium. (Wackenroder.)

5. *White Flux, Fluxus albus.* Formed by igniting a mixture of equal parts of tartar and nitrate of potash.—The mass thus obtained is white; because in this proportion the oxygen of the nitric acid contained in the nitre is more than sufficient for the combustion of the carbon of the tartaric acid in the tartar; but for that very reason the residue contains a considerable quantity of nitrite and likewise some nitrate of potash.

6. *Nitrum fixum.* Obtained by detonating nitre with charcoal.—Either powdered charcoal is thrown by degrees upon nitre fused in a crucible, until it no longer detonates, or a mixture of about 3 parts of nitre and 1 part of powdered charcoal is thrown by small portions into a red-hot crucible and kept at red heat for some time. The mass contains nitrite of potash and cyanide of potassium, besides sulphate of potash, chloride of potassium, lime and silicate of potash (partly derived from the charcoal, and partly from the crucible.) (Wackenroder.)

7. Acetate of potash is heated to redness, and the carbonaceous mass exhausted with water.—For this purpose, pure acetate of potash is prepared by one of the following methods:—*a.* Distilled vinegar is saturated with pearl-ash, the sulphuric and hydrochloric acids present, separated by the addition of acetate of baryta and acetate of silver, and the filtrate evaporated to dryness. (Dulk & Gruber.) The carbonate of potash, however, which remains after heating the residue to redness, takes up, when dissolved in water, a considerable quantity of the carbonate of baryta produced at the same time; the lime and silica also contained in the pearl-ash are not separated by this process. (Wackenroder.)—*b.* Acetate of lead is decomposed by an equivalent quantity of salt of tartar [or sulphate of potash]. The filtrate, evaporated and heated to redness in a silver crucible yields a pure product. (Wackenroder.)

8. By igniting oxalate of potash. Potash-ley is boiled down till the carbonate of potash crystallizes; the crystals obtained on cooling are dissolved in 2 parts of water, and saturated with ordinary oxalic acid; and the simple oxalate of potash thus formed is purified by filtration and crystallization: 3 parts of the crystals are then dissolved in 6 parts of water, and 2 parts of oxalic acid dissolved in 4 parts of water added while the liquid is hot; the binoxalate of potash, which crystallizes out as the mixture cools, is collected on a filter, washed with water till a solution of silver remains unaffected by the liquid which passes through, and then thrown into a red-hot platinum or silver crucible. In this way, perfectly pure carbonate of potash is obtained. (Duflos, *N. Br. Arch.* 23, 305.)

9. By heating bicarbonate of potash.—As the bicarbonate of potash is usually prepared from crude potash ley, it still contains silica; it must not, therefore, be heated to full redness in the silver crucible usually employed, lest the silica should again combine with the potash. When the salt, is dissolved in water, the silica is left behind. (Berzelius.) Wackenroder found that carbonate of potash thus prepared still contained a con-

siderable quantity of silica and chloride of potassium, but neither lime nor magnesia.

10. Carbonate of potash is thrown down from an alcoholic solution of the acetate by passing carbonic acid gas through it. Landmann (*Bull. de la Soc. imp. de Mosc.* 1838, 58; also *Pogg.* 46, 650) burns sulphate of potash with ¼ of its weight of charcoal; dissolves the sulphide of potassium thus obtained, in wood-vinegar; skims off the tar; boils the solution with water and charcoal obtained from animal matter; evaporates the filtrate to dryness; fuses the salt at a gentle heat in iron vessels, so that no acetic acid may be driven off; dissolves the fused mass when cool in water; filters; evaporates to dryness; dissolves the remaining white salt in alcohol, to saturation; and passes a stream of carbonic acid gas through the liquid: by this treatment carbonate and bi-carbonate of potash are precipitated. The precipitate, when pressed and fused, affords pure carbonate of potash. Acetic ether may be prepared from the filtrate. Wackenroder gives the preference to the third method.

*Impurities found in carbonate of potash.—Sulphate of potash:* Turbidity produced on adding chloride of barium with excess of hydrochloric acid.—*Chloride of potassium:* Cloud with nitrate of silver and nitric acid in excess.—*Phosphate of potash:* Floculent precipitate on the addition of a little chloride of calcium and excess of ammonia, after long boiling with excess of hydrochloric acid to expel all the carbonic acid.—*Nitrate or nitrite of potash:* The solution of the salt in excess of sulphuric acid turns reddish when solution of ferrous sulphate is poured upon it.—*Cyanide of potassium:* Prussian-blue formed on the addition of ferroso-ferric sulphate and excess of hydrochloric acid.—*Soda:* On saturating the carbonate of potash with acetic acid, evaporating to dryness, dissolving the residue in alcohol, precipitating the potash with bichloride of platinum, evaporating the filtrate mixed with sulphuric acid, igniting the residue, exhausting it with water, concentrating the solution by evaporation, and leaving it to cool, crystals of sulphate of soda are obtained, easily recognized by their form.—*Carbonate of lime:* Dissolves in water, partly through the medium of the carbonate of potash. A solution of this kind, when left to stand for some time, yields a crystalline deposit of carbonate of lime; it also gives a cloud with oxalic acid, after neutralization with acetic acid.—*Silica:* Partly remains undissolved when the salt is digested in water; partly dissolves, often in large quantity, in the form of silicate of potash. This solution, supersaturated with hydrochloric acid, yields, if it be rich in silica, a gelatinous precipitate of that substance, at least when evaporated; in any case, the mixture, when evaporated to dryness and then digested in water to dissolve the chloride of potassium, leaves a residue of silica.—*Oxide of copper:* The salt neutralized with acetic acid gives the reactions of copper.

White, solid mass, of specific gravity about 2·2643. (Karsten.) Fusible at a bright red heat; volatile at a white heat. Tastes strongly alkaline; exerts an alkaline reaction on vegetable colours, but is only slightly corrosive.

| | Calculation. | Vauquelin. | Longchamp. | Ure. | Dalton. | Bérard. |
|---|---|---|---|---|---|---|
| KO | 47·2 .... 68·2 | .... 67 | .... 67·59 | .... 68·6 | .... 68·9 | .... 70·21 |
| $CO^2$ | .... 22·0 .... 31·8 | .... 33 | .... 32·41 | .... 31·4 | .... 31·1 | .... 29·79 |
| | 69·2 .... 100·0 | .... 100 | .... 100·00 | .... 100·0 | .... 100·0 | .... 100·00 |

The salt is decomposed at a red heat, by vapour of water, yielding hydrate of potash and carbonic acid gas. (Gay-Lussac & Thénard.)

Heated to whiteness with 2 atoms of charcoal, it yields carbonic oxide gas and potassium; heated to redness with silica, it yields carbon, carbonic oxide gas, and silicate of potash.

*Carbonate of Potash with 2 atoms of water:* crystallizes from a concentrated aqueous solution of salt of tartar or pearl-ash, on long standing. Indistinct rhombic octohedrons with truncated summits (*Fig.* 42); the angles of the rhomb, = 122° and 58° (*Comp.* Bérard, *Ann. Chim.* 71, 50; Giese, *Scher. Ann.* 4, 294; Fabroni, who erroneously considers himself the discoverer, *Ann. Chim. Phys.* 25, 5; Phillips, *Phil. Mag. Ann.* 1, 468; Wackenroder, *Kastn. Arch.* 11, 222; Planche & Lecann, *J. Pharm.* 12, 337.)

| | Calculation. | | Giese. | Bérard. | Phillips. |
|---|---|---|---|---|---|
| KO | 47·2 | 54·13 | 55 | 79·4 | 79 |
| $CO^2$ | 22·0 | 25·23 | 25 | | |
| 2HO | 18·0 | 20·64 | 20 | 20·6 | 21 |
| KO,$CO^2$,2HO | 87·2 | 100·00 | 100 | 100·0 | 100 |

*Aqueous Carbonate of Potash; Oil of Tartar, Oleum tartari per deliquium, Liquor nitri fixi.* Both the anhydrous and the crystallized salt deliquesce rapidly in the air and form an oily liquid.—10 parts of dry carbonate of potash exposed for 42 days to an atmosphere saturated with moisture, attract 36 parts of water. (Brandes, *Schw.* 51, 423.) 1 part of carbonate of potash requires for solution at 3° (37·4° F.), 1·05 parts of water; at 6° (42·8 F.), 0·962 parts; at 12·6° (54° F.), 0·9 parts; at 26° (78·8 F.), 0·747 parts; and at 70° (158° F.), 0·49 parts of water. (Osann.) The specific gravity of the most concentrated solution, containing 48·8 per cent. of salt, is 1·54, and its boiling point 113° (235·4 F.)—*Dalton.*

*Amount of Anhydrous Salt contained in an Aqueous Solution of Carbonate of Potash, according to Tünnerman.* (*N. Tr.* 18, 2, 20), at 15° (59° F.).

| Sp. gr. | Per cent. | Sp. gr. | Per cent. | Sp. gr. | Per cent. | Sp. gr. | Per cent. |
|---|---|---|---|---|---|---|---|
| 1·4812 | 40·504 | 1·3585 | 30·349 | 1·2282 | 19·580 | 1·0940 | 8·811 |
| 1·4750 | 40·139 | 1·3480 | 29·360 | 1·2150 | 18·601 | 1·0829 | 7·832 |
| 1·4626 | 39·160 | 1·3378 | 28·391 | 1·2020 | 17·622 | 1·0719 | 6·853 |
| 1·4504 | 38·181 | 1·3277 | 27·412 | 1·1892 | 16·643 | 1·0611 | 5·874 |
| 1·4384 | 37·202 | 1·3177 | 26·432 | 1·1766 | 15·664 | 1·0505 | 4·895 |
| 1·4265 | 36·223 | 1·3078 | 25·454 | 1·1642 | 14·685 | 1·0401 | 3·916 |
| 1·4147 | 35·244 | 1·2980 | 24·475 | 1·1520 | 13·706 | 1·0299 | 2·934 |
| 1·4030 | 34·265 | 1·2836 | 23·496 | 1·1400 | 12·727 | 1·0108 | 1·958 |
| 1·3915 | 33·286 | 1·2694 | 22·517 | 1·1282 | 11·748 | 1·0098 | 0·979 |
| 1·3803 | 32·307 | 1·2554 | 21·538 | 1·1166 | 10·769 | 1·0048 | 0·489 |
| 1·3692 | 31·328 | 1·2417 | 20·539 | 1·1052 | 9·790 | | |

*b.* Sesqui-carbonate of Potash?—An aqueous solution of bi-carbonate of potash boiled as long as it evolves carbonic acid—or a solution of 1 atom of carbonate and 1 atom of bi-carbonate of potash in hot water—yields, on cooling, crystals of the sesqui-salt; these crystals are deliquescent in the air, and insoluble in alcohol. (Berthollet; Berzelius, *Lehrb.* 4, 104.) According to H. Rose's experiments, the existence of this salt is doubtful (*vid.* III. p. 25).

*c.* Bi-carbonate of Potash. — *Berthollet's neutral carbonate of potash.*—Known only in combination with water.—1. When a concentrated solution of simple carbonate of potash is saturated with carbonic acid gas, *the greater part of the* more difficultly soluble bi-acid salt crystallizes out,

The carbonic acid gas generated during the fermentation of wine, may be conducted into the potash-ley by means of a connecting tube; or the ley may be placed in an open vessel in the space filled with carbonic acid gas over the fermenting liquid: or the carbonic acid gas may be evolved from chalk, marble, &c., by means of diluted sulphuric or hydrochloric acid. The gas is first conducted through a bottle half full of water, to free it from any impurities mechanically carried over, and then into the potash-ley. This is contained either in a number of Woulfe's bottles connected by bent tubes, or in one large vessel. The apparatus may be so arranged, that the carbonic acid shall be given off exactly at the same rate as it is absorbed. The gas may be evolved either from the gas-generating vessel of Mohr (*App.* 44, described II. 92), or from a Woulfe's bottle filled with pieces of chalk, and having a narrow bent tube fitted into one of its mouths, the inner end reaching to the bottom of the bottle, whilst the outer end passes into a vessel containing common dilute hydrochloric acid. The carbonic acid gas is formed at first so rapidly and in such abundance, that the air is driven out of all the bottles through the open mouth of the last, and the whole space becomes filled with carbonic acid gas. This opening is hereupon closed.

In proportion as the gas is absorbed, either an additional quantity of hydrochloric acid passes into the Mohr's bottle, or the acid passes through the bent tube into the Woulfe's bottle filled with chalk, and developes more carbonic acid.—The bent tubes which conduct the gas should not be in contact with the potash solution, because they would quickly be stopped up by the bicarbonate crystallizing within them; besides, finer and larger crystals are formed when the solution is not disturbed by bubbles of gas.—The absorption always proceeds slowly, but more quickly in proportion to the concentration of the solution; large quantities require a week to saturate them completely.—From common potash-ley, carbonic acid at first throws down a large quantity of silica, which can only be partially separated from the crystals, by stirring and decanting the solution. It is well, therefore, before using the potash-ley, to free it from the silica by means of charcoal.—If the crystals contain silica, they must be dissolved in water at 60°, (140° F.) to saturation, filtered and crystallized by cooling to a low temperature. Much loss is however sustained by this mode of proceeding; because, while the salt is dissolving, carbonic acid passes off, and simple carbonate is formed; and a further and proportionally greater loss is incurred on endeavouring to recover the remainder of the salt by gently evaporating the mother liquor. (*Vid.* Weitzel, *Ann. Pharm.* 4, 80; Mohr, *Ann. Pharm.* 29, 268.)

2. Solid carbonate of potash, slightly moistened, is saturated with carbonic acid.—Wöhler (*Ann. Pharm.* 24, 49) burns tartar in a covered crucible, moistens the carbonaceous mass when cold with a little water, puts it into a suitable vessel, and passes carbonic acid gas through it to saturation. Absorption takes place very rapidly, and with great rise of temperature; hence the vessel must be surrounded with cold water. The mass is then exhausted with a little water at 60° (140° F.), filtered, and allowed to cool, when most of the salt separates in large crystals.—Duflos (*N. Br. Arch.* 23, 305) evaporates to dryness a mixture of 3 parts of carbonate of potash, 1 part of starch, and 4 parts of water; heats it to redness; and treats the carbonaceous residue by Wöhler's method.—Creuzburg (*Kastn. Arch.* 17, 252) reduces the half dry carbonate of potash to powder, moistens the mass with alcohol, and exposes it to carbonic acid gas; the gas is absorbed with great rise of temperature, and

the salt bakes together into a dry mass. This is broken up, moistened with very dilute alcohol, and again exposed to the gas, by which it becomes completely saturated.

3. A concentrated solution of carbonate of potash is heated with sesquicarbonate of ammonia, whereupon caustic ammonia is given off. (Cartheuser, *Acta Ac. El. Mogunt.* 1757, 1, 149.) The operation is conducted in a retort, that the ammonia may be collected.—Duflos (*Br. Arch.* 29, 50) heats the filtered solution of 4 parts of carbonate of potash in 4 parts of water, in a flask immersed in a boiling water bath—adds 1 part of ordinary carbonate of ammonia in lumps—places the head on—boils for an hour or more—leaves the solution to cool, and collects the crystals. The mother-liquor is again treated in the same manner with 1 part of carbonate of ammonia, and yields as large a crop of crystals as before; and an additional quantity on being evaporated and cooled. The total quantity obtained is $4\frac{2}{3}$ parts.—Bucholz (*Taschenb.* 1817, 148) and Trommsdorff (*N. Tr.* 17, 1, 17) obtained but a small quantity of crystals by this method.

4. A concentrated solution of carbonate of potash, heated to 75° (167° F.), is mixed with barely half as much acetic acid or cream of tartar, as would be required to saturate the whole of the potash; the acid being added by degrees, till the solution begins to effervesce strongly; it is then filtered. A considerable quantity of bicarbonate crystallizes out on cooling. (Sehlmeyer, *Kastn. Arch.* 2, 495—Fölix, *Br. Arch.* 38, 151.)

The crystals obtained by either of these methods are washed with a little cold water, and then dried by gentle pressure between folds of bibulous paper.

Large transparent crystals belonging to the oblique prismatic system. Primary form; a right rhomboidal prism (Fig. 90). Cleavage-planes parallel to *t*, *i*, and *l*. $t:f$ backwards $= 127° 35'$; $t:i = 126° 45'$; $t:l = 103° 25'$; $l:i = 156° 50'$; $l:f = 128° 50'$; $i:f = 105° 40'$; $t:u = 111°$; $u:u = 138°$. The increase of the *i* surface often causes the *l* and *f* surfaces to disappear. (Brook, *Ann. Phil.* 22, 42.) Tastes saline, slightly alkaline, but no longer caustic; its reaction is slightly alkaline.

| | Calculation. | | Bergman. | Vauquelin. | Kirwan. | Pelletier. | Val.Rose. | Bérard. |
|---|---|---|---|---|---|---|---|---|
| KO | 47·2 | 47·1 | 48 | 46 | 41 | 40 | 53 | 48·92 |
| $2CO^2$ | 44·0 | 43·9 | 20 | 47 | 43 | 43 | 43 | 42·01 |
| HO | 9·0 | 9·0 | 32 | 7 | 16 | 17 | 4 | 9·07 |
| Crystallized | 100·2 | 100·0 | 100 | 100 | 100 | 100 | 100 | 100·00 |

The crystals, when dry, remain unaltered in the air. In vacuo over oil of vitriol, they lose in 24 hours only 0·05 per cent., and in an air-tight bell-jar over hydrate of potash, 0·47 per cent. of water. (H. Rose.) When strongly heated, they lose half their acid, together with the water. When the salt is dissolved in water, it gives up the half of its acid much more readily.—A cold dilute solution placed by itself under an exhausted receiver evolves bubbles of carbonic acid, amounting, with frequent exhaustion, to 4·52 per cent. in 20 hours. If there be placed in the vacuum a vessel containing oil of vitriol diluted with so much water that it will not cause the liquid to solidify, the solution emits large bubbles of gas, and yields distinguishable crystals of carbonate and bicarbonate of potash (but no sesquicarbonate), in about equal quantities. A solution of these mixed crystals in water again placed in vacuo, still emits bubbles of carbonic acid; but not a third time. After this, the salt is found to have lost 10·62 per cent. of carbonic acid, and by continually repeating this

treatment, simple carbonate of potash would at length be obtained alone. By evaporation to dryness over oil of vitriol in a receiver containing air, at a temperature between 15° and 18°, the solution also loses 6·36 per cent. of carbonic acid; if the receiver contains hydrate of potash as well as oil of vitriol, the loss of carbonic acid amounts, after the evaporation to dryness, to 18·25 per cent., or nearly half.—A solution of bicarbonate of potash boiled in the air, loses in half an hour, 11·85 per cent.; after long boiling—the water being replaced as it evaporates—almost the half of the carbonic acid goes off, so that scarcely anything but simple carbonate remains. When the liquid is boiled under strong pressure, the loss of carbonic acid in the same time is less. (H. Rose, *Pogg.* 34, 149.)—This salt dissolves in 4 parts of cold, in $\frac{5}{6}$ parts of boiling water, and 1200 parts of hot alcohol. (*Vid.* Bergmann, *Opusc.* 1, 13;—Berthollet, *N. Gehl.* 3, 257.)

### Potassium and Boron.

A. *Boride of Potassium*?—According to Sir H Davy, these two elements unite without inflammation, and form a grey metallic mass, which conducts electricity, and is decomposed by contact with water, yielding potash and hydride of boron. According to Gay-Lussac & Thénard, the product obtained by heating the two elements, is not a chemical compound, but only a mixture.

### B. Borate of Potash.

*a.* Monoborate.—When 100 parts of boracic acid are heated to redness with excess of carbonate of potash, a quantity of carbonic acid is given off, as much, namely, as was previously combined with 139 parts of potash. (Arfvedson).—The compound is obtained pure, by fusing together one atom (= 34·8 parts of vitrefied or 61·8 parts of crystallized) boracic acid with one atom ( = 69·2 parts) of dry carbonate of potash. It is fusible at a strong white heat—difficultly soluble in water—and does not crystallize from the solution; has a distinctly caustic alkaline taste—and absorbs carbonic acid from the air, till it is converted into a mixture of one atom of carbonate of potash, and one atom of biborate of potash. (Berzelius, *Pogg.* 34, 568.)

*b.* Biborate.—A solution of carbonate of potash is supersaturated with boracic acid at a boiling heat, and solution of potash added till the liquid becomes alkaline; it is then left to crystallize. At first, the salt *d* crystallizes out, and then from the mother-liquor the salt *b*.—Crystallizes in regular six-sided prisms, acute rhombohedrons with the lateral vertices often truncated, and double six-sided pyramids. (*Fig.* 135, 151, 154, and 131.) Tastes slightly alkaline; reddens turmeric; swells in the fire like borax, and then fuses to a clear glass; dissolves readily in hot and cold water. (Gm.; Laurent.)

| | Calculation. | | Arfvedson. | | Calculation. | | Laurent. |
|---|---|---|---|---|---|---|---|
| KO | 47·2 | 57·56 | 58·16 | KO | 47·2 | 29·17 | 28·5 |
| $BO^3$ | 34·8 | 42·44 | 41·84 | $2BO^3$ | 69·6 | 43·02 | 43·7 |
| | | | | 5HO | 45·0 | 27·81 | 27·8 |
| *a.* | 82·0 | 100·00 | 100·00 | *b.* Cryst. | 161·8 | 100·00 | 100·0 |

*c.* TERBORATE.—Forms sometimes on the surface of the foregoing solution in rectangular prisms, terminated with four-sided summits which are set upon the lateral edges (therefore with the *m*, *t*, and *a*, faces of the right prismatic system). Unaltered in the air; fuses easily, and at the same time froths up. (Laurent.)

*d.* SEXBORATE.—Crystallizes from the solution when it is neutral, or when it reddens litmus.—Right rectangular prisms, terminated by four or six-sided summits, mostly hemitropic. Very brilliant. Turns reddened litmus slightly blue. Permanent in the air. Dissolves sparingly in cold, freely in boiling water. The solution coloured blue with tincture of litmus, assumes a wine-red colour on the addition of a little sulphuric acid, which sets free the boracic acid. It is not till all the potash is saturated with sulphuric acid, that a drop of the tincture produces the bright red colour. (I., 152; Laurent, *Ann. Chim. Phys.* 67, 215; also *Ann. Pharm.* 28, 89; also *J. pr. Chem.* 14, 506.)

| | Calculation. | | Laurent. | | Calculation. | | Laurent. |
|---|---|---|---|---|---|---|---|
| KO | 47·2 | 21·11 | 21·6 | KO | 47·2 | 13·64 | 14·0 |
| $3BO^6$ | 104·4 | 46·69 | 46·4 | $6BO^6$ | 208·8 | 60·35 | 60·8 |
| 8HO | 72·0 | 32·20 | 32·0 | 10HO | 90·0 | 26·01 | 25·2 |
| *c.* Cryst. | 223·6 | 100·00 | 100·0 | *d.* Cryst. | 346·0 | 100·00 | 100·0 |

## POTASSIUM AND PHOSPHORUS.

A. PHOSPHIDE OF POTASSIUM.—1. Potassium unites with phosphorus when gently heated with it in a vessel containing nitrogen, the combination being attended with evolution of light and heat. (Gay-Lussac and Thénard.) Under rock-oil, the combination takes place without combustion, merely causing the oil to boil. (Magnus, *Pogg.* 17, 527.)—2. Heated potassium withdraws the phosphorus from phosphuretted hydrogen gas. (Gay-Lussac & Thénard.)—3. Potassium heated with glacial phosphoric acid, yields a red mass, which, when mixed with water, gives off the less inflammable phosphuretted hydrogen. (Gay-Lussac & Thénard.) Probably a mixture of phosphide of potassium and phosphate of potash.—To obtain this compound pure, potassium must be heated with excess of phosphorus in a thin glass flask, through which a current of dry hydrogen gas is passed, till flame is produced, and further till the excess of phosphorus is volatilized. (H. Rose, *Pogg.* 12, 547.)

Dark chocolate-brown substance without metallic lustre. (Gay-Lussac & Thénard.) When excess of potassium is present, the compound is dark-grey, and possesses metallic lustre (H. Davy); copper-red, having the metallic lustre; crystalline; emitting bubbles when crystallized after fusion (H. Rose); when prepared under rock-oil it is dark-yellow and spongy. (Magnus.)—Heated in the air, it burns with lively inflammation and forms phosphate of potash. (H. Davy.)—With water it is decomposed into phosphuretted hydrogen, hypophosphite of potash, and solid phosphide of hydrogen. The evolution of the phosphuretted hydrogen is followed by a sort of explosion. This gas is sometimes easily inflammable, sometimes difficultly so; and its volume is greater than that of the hydrogen which the potassium contained in the compound would of itself have evolved. If the vessel filled with hydrogen gas, in which the phosphide of potassium was prepared, be opened under water, so that only the vapour of water comes in contact with the phosphide, decomposition pro-

ceeds gradually, with the production of spontaneously inflammable phosphuretted hydrogen gas; from the decomposed mass water dissolves, hypophosphite of potash quite free from phosphate, and separates a yellow powder, which, on being heated, melts and assumes the appearance of phosphorus. (H. Rose.) This yellow powder is solid phosphide of hydrogen. (H., Magnus.)

B. Compound of Potash and Phosphoric Oxide.—Phosphoric oxide covered with a solution of potash, becomes black by combining with the potash, but quickly passes into phosphuretted hydrogen gas and phosphate of potash.—A small quantity of the oxide dissolves in absolute alcohol which contains a little potash, producing a bright-red solution, and is again thrown down as hydrate by weak sulphuric acid. (A solution richer in potash would soon effect a decomposition into phosphuretted hydrogen and phosphate of potash.) If more phosphoric oxide is added to the red solution, it becomes coloured brown without dissolving; and a further addition of oxide throws down all that was previously dissolved. Hence the compound of potash with a little phosphoric oxide is soluble in alcohol, but not that which contains a larger quantity of the oxide. The last mentioned brown compound is decomposed during washing — even with absolute alcohol—into phosphate of potash and oxide of phosphorus, becoming colourless at the same time. (Leverrier, *Ann. Chim. Phys.* 65, 266.)

C. Hypophosphite of Potash.—Phosphate of lime is decomposed by carbonate of potash, the filtrate evaporated to dryness at a gentle heat, the hypophosphite of potash extracted from the residue by means of alcohol, and the solution evaporated in vacuo over oil of vitriol.—2. Solution of potash is boiled with phosphorus, and left to evaporate slowly in the air, so that the excess of caustic potash may be saturated with carbonic acid; the residue is exhausted with alcohol, and the solution placed in vacuo.—3. An alcoholic solution of potash is boiled with phosphorus, the liquid poured off from the phosphorus undissolved, and—if much salt has crystallized out—the mass treated with more alcohol in order to redissolve it; powdered bi-carbonate of potash is then added, to convert the excess of caustic potash into carbonate; and, after some time, the solution is decanted and the alcohol distilled off. (H. Rose, *Pogg.* 12, 84, 32, 467.) In the same manner this salt was earlier obtained by Grotthuss (*Ann. Chim.* 64, 20), and Sementini (*Schw.* 17, 384). The latter regards it as phosphide of potash. According to him, it is prepared either by placing sticks of phosphorus in a saturated alcoholic solution of potash, and leaving them for a fortnight till no more phosphuretted hydrogen is developed—whereupon, the hitherto oily liquid becomes limpid, and deposits a red powder together with a part of the salt in scales: the rest may be obtained by evaporation;—or by mixing a concentrated aqueous solution of potash, first with pieces of phosphorus and then with alcohol: the addition of the alcohol causes evolution of phosphuretted hydrogen.

White, opaque, confused crystalline mass (Sementini).—Heated to redness out of contact of air, it evolves easily inflammable phosphuretted hydrogen, and leaves hypophosphate of potash. (H. Rose.) Burns with a yellow flame if heated in the air. Detonates violently when evaporated to dryness in contact with nitric acid. (Sementini.) Very soluble in water and alcohol; deliquesces in the air more rapidly than chloride of calcium. (Dulong.)

D. Phosphite of Potash. — Phosphorous acid neutralized with potash yields in vacuo a thick syrup, in which small crystals are found. (H. Rose, *Pogg.* 9, 28.) Not crystallizable, deliquescing in the air, insoluble in alcohol. (Dulong.) Fourcroy & Vauquelin, who sought to produce this salt by the combination of potash with phosphorous acid prepared by the slow combustion of phosphorus and containing much phosphoric acid, obtained rectangular four-sided crystals with dihedral summits—having a sharp and saline taste—containing 49·5 potash, 39·5 phosphorous (?) acid, and 11·0 water,—unaltered in the air,—decrepitating in the fire, and then melting with slight phosphorescence,—soluble in 3 parts of cold and in a smaller quantity of hot water. [Was this biphosphate of potash?]

## E. Ordinary or Terbasic Phosphate of Potash.

*a.* Basic or Tri-Phosphate.—One atom of phosphoric acid heated with excess of carbonate of potash, evolves 3 atoms of carbonic acid, and consequently takes up 3 atoms of potash. (Mitscherlich.)—Obtained by strongly heating phosphate of potash with hydrate of potash.—White mass, fusing at a gentle red heat to a clear glass, which, on cooling, always becomes opaque.—It dissolves almost entirely in hot water, and separates on cooling in crystalline grains. With phosphoric, hydrochloric, and nitric acids it readily forms a glutinous liquid, from which, after some degree of concentration, it separates, on the addition of alkalis, in a granular form. (Darracq, *Ann. Chim.* 40, 176.) By strongly heating 2 parts of chlorate of potash with 1 part of (syrupy?) phosphoric acid, and exhausting the mass with water, Darracq obtained this salt as an insoluble residue. (Should not this be metaphosphate of potash?)—The solution obtained from phosphoric acid fused with excess of carbonate of potash, yields small needles, very soluble in water, but not altogether deliquescent. (Graham, *Pogg.* 32, 47.)

| | Calculation. | | Saussure. |
|---|---|---|---|
| 3KO ..... | 141·6 ..... | 66·48 ..... | 65 |
| $cPO^5$ ..... | 71·4 ..... | 33·52 ..... | 35 |
| $3KO,cPO^5$ ..... | 213·0 ..... | 100·00 ..... | 100 |

*b.* Neutral or Di-Phosphate.—$2KO,HO,cPO^5$. Cannot be obtained in a crystalline form. (Graham.) The square octahedrons which Thomson asserts he obtained of this salt, belong probably to the salt *c*.—This salt in solution is decomposed by sulphate and hydrochlorate of ammonia, by double affinity. (Funcke, *N. Tr.* 8, 2, 60.)

*c.* Monophosphate.—*Acid Phosphate.*—Phosphoric acid is added to neutral phosphate or carbonate of potash, till the liquid reddens litmus paper; on drying, however, the paper again becomes blue. When solution of phosphoric acid is exactly neutralized with potash and evaporated till crystallization commences, acid phosphate of potash crystallizes out, and the mother-liquor possesses an alkaline reaction. (Mitscherlich.)—Crystalline system, the square prismatic. (*Fig.* 23 and 30.) The crystals of *Fig.* 23 form best in a solution which, at the same time, contains neutral phosphate of potash. $e : e^1 = 122° 16'$ (122° 2′ Brooke); $e : e^2 = 86° 24'$; $e : r = 133° 12'$ (133° 15′ Brooke); $r : r = 90°$. (Mitscherlich.) As the crystals contain only 2 atoms of basic water and no water of crystallization ($KO,2HO,cPO^5$), they continue clear even at 204°. (Graham.)

This salt melts in the fire to a clear glass of metaphosphate of potash, which, however, becomes opaque on cooling. It tastes very acid, and strongly reddens litmus paper, though the redness disappears on drying. Easily dissolved by water; insoluble in alcohol. (Vauquelin, *Ann. Chim.* 74, 96; Mitscherlich, *Ann. Chim. Phys.* 19, 364; Brooke, *Ann. Phil.* 23, 480.)

| | Calculation. | | Mitscherlich. | | Calculation. | | Mitscherlich. |
|---|---|---|---|---|---|---|---|
| KO | 47·2 | 39·8 | 39·64 | KO | 47·2 | 34·55 | 86·26 |
| $PO^5$ | 71·4 | 60·2 | 61·39 | $cPO^5$ | 71·4 | 52·27 | |
| | | | | 2HO | 18·0 | 13·18 | 13·74 |
| *c*. Fused | 118·6 | 100·0 | 101·03 | Crystallized | 136·6 | 100·00 | 100·00 |

## F. Pyrophosphate of Potash.

*a*. Neutral Pyrophosphate, $2KO, bPO^5$.—1. Obtained by heating E, *b*, to redness. The salt dissolved in water does not crystallize on evaporation, but is reconverted into E, *b*, by combining with one atom of basic water. (Graham.)—¶ 2. By treating an alcoholic solution of potash with a slight excess of ordinary phosphoric acid, and afterwards adding alcohol till the liquid becomes milky: in the course of 24 hours, a dense acid syrup separates, which is a mixture of $2KO, HO, PO^5$ and $KO, 2HO, PO^5$. The syrupy mixture is then evaporated to dryness in a platinum dish and ignited, whereby a mixture is obtained consisting of pyrophosphate and metaphosphate of potash, which can readily be separated in consequence of the insolubility of the latter salt in water. Pyrophosphate of potash, after ignition, forms a white fused mass, which deliquesces very rapidly in the air; its aqueous solution has an alkaline reaction, and may be boiled without being converted into ordinary phosphate. This change takes place however when the solution of the salt is boiled with caustic potash. When a syrupy solution of pyrophosphate of potash is evaporated over oil of vitriol, it solidifies to a brilliant white radiated mass $= 2KO, PO^5 + 3Aq$. One atom of water is driven off below 100°, but the salt is rendered anhydrous only at a temperature of 300°. (Schwarzenberg, *Ann. Pharm.* 55, 133.)

| | Calculation. | | Schwarzenberg. | | Crystallized. | | | Schwarzenberg. |
|---|---|---|---|---|---|---|---|---|
| 2KO | 94·4 | 56·93 | 56·71 | 2KO | 165·8 | 86 | | 85·89 |
| $bPO^5$ | 71·4 | 43·07 | 42·71 | $bPO^5$ | | | | |
| | | | | 3HO | 27·0 | 14 | | 14·11 |
| $2KO, bPO^5$ | 165·8 | 100·00 | 99·42 | | 192·8 | 100 | | 100·00 |

*b*. Acid Pyrophosphate.—The neutral salt is dissolved in acetic acid and alcohol added; acid pyrophosphate of potash separates in the form of a syrupy liquid, leaving acetate of potash dissolved in the alcohol.

$$2KO, PO^5 + \overline{Ac}HO = KO, HO, PO^5 + KO, \overline{Ac}.$$

—The syrupy liquid is washed several times with alcohol and placed in a basin over oil of vitriol; it solidifies in a few days to a white deliquescent mass. The aqueous solution is acid to test paper, and may be boiled without being changed into the ordinary phosphate.

| | Calculation. | Schwarzenberg. |
|---|---|---|
| KO | 47·2 | 37·14 |
| HO | 9·0 | 7·13 |
| $bPO^5$ | 71·4 | 55·73 |
| $KO, HO, bPO^5$ | 127·6 | 100·00 |

(Schwarzenberg, *Ann. Pharm.* 65, 133.) ¶

G. Metaphosphate of Potash.—KO, $\alpha PO^5$.

1. Acid phosphate of potash E, *c*, gradually heated to above 204° (399·2° F.) undergoes semifusion and becomes partly soluble in water. If heated almost to redness, it is rendered wholly insoluble; and if then fused and raised to a white heat, it undergoes no further change. Water boiled for an hour with the powdered salt dissolves nothing. Graham does not precisely explain whether he considers this substance as the metaphosphate of potash or not.—2. The salt obtained in solution from a mixture of aqueous metaphosphoric acid and potash is permanent, but not crystallizable. (Graham, *Pogg.* 32, 64.)

¶ 3. When a mixture of equal parts of chlorate of potash and syrupy phosphoric acid is strongly ignited, and the residue digested with water, metaphosphate of potash remains in the form of an anhydrous compound, nearly insoluble in water, but dissolving in acids, whether concentrated or dilute. The acetic acid solution gives a white precipitate with nitrate of silver.

| | Calculation. | | Maddrell. |
|---|---|---|---|
| KO | 47·0 | 39·8 | 39·645 |
| $PO^5$ | 71·4 | 60·2 | 60·355 |
| KO, $PO^5$ | 118·4 | 100·0 | 100·000 |

(Maddrell, *Mem. Chem. Soc.* 3, 373.)

Potassium and Sulphur.

Potassium unites with sulphur by the application of a gentle heat, the combination being attended with vivid inflammation. (H. Davy, Gay-Lussac, & Thénard.) In this manner, 1 atom of potassium combines with at least 1 atom, and at most 5 atoms, of sulphur. (Berzelius.)

A. Monosulphide of Potassium.—1. Hydrogen gas is passed over sulphate of potash at a red heat. (Berzelius.)

$$KO, SO^3 + 4H = KS + 4HO.$$

—The glass or porcelain tube is attacked in this operation from the formation of silicate of potash, and thereby much hydrosulphuric acid is evolved. (Berzelius, Regnault, *Ann. Chim. Phys.* 62, 386.)—2. 87·2 parts (1 At.) of sulphate of potash are heated to bright redness, with rather more than 24 parts (4 At.) of charcoal, or in a charcoal crucible. (Berthier.) If the heat is not sufficient, about $\frac{1}{5}$ of the potash remains undecomposed, and a mixture is formed of potash with a sulphide of potassium containing more than one atom of sulphur. (Gay-Lussac.) If an excess of carbon is not used, the product consists of sulphide of potassium having more than one atom of sulphur, and carbonate of potash. (Wittstock.)—3. Also according to Berzelius, when sulphur is gently heated (at a temperature of 105°, *Fordos & Gelis*) with excess of hydrate of potash, the mixture boils up and monosulphide of potassium is formed, mixed however with hyposulphite of potash.

$$3(KO, HO) + 4S = 2KS + KO, S^2O^2 + 3HO.$$

—The sulphide obtained by the first process is of a light cinnabar-red colour, with a crystalline fracture, becoming dark with heat, and melting below redness, after which it appears black and opaque. (Berzelius.) That *obtained by the second* process is of a beautiful flesh colour, translucent,

irregularly crystalline, and volatile at a red heat. (Berthier, *Ann. Chim. Phys.* 22, 233.)

| | | Calculation. | |
|---|---|---|---|
| K | 39·2 | | 71·01 |
| S | 16·0 | | 28·99 |
| KS | 55·2 | | 100·00 |

This substance burns very slowly at a red heat in the air, because it quickly becomes covered with a crust of sulphate of potash. (Berzelius; Berthier.) Sulphide of potassium is deliquescent in the air; that obtained by the second method dissolves in water with considerable rise of temperature, so that any portion of carbon still mixed with it becomes luminous on moistening the mass. The solution contains either hydrated sulphide of potassium, or monohydrosulphate of potash: or, according to H. Rose's supposition (*Pogg.* 55, 533), one atom of free potash with one atom of the double sulphide of hydrogen and potassium:

$$2KS + HO = KO + KS,HS;$$

or bihydrosulphate of potash. (II., 225, 226.) The same solution is obtained by dividing a solution of potash into two equal parts, saturating one part with hydrosulphuric acid, out of contact of air, freeing the solution from the excess of hydrosulphuric acid absorbed by the water, and then mixing it with the other part. The solution is a colourless liquid, having an alkaline and bitter taste, a highly alkaline reaction and corrosive properties; mixed with hydrochloric acid, it evolves sulphuretted hydrogen without depositing sulphur; it likewise exhibits the decompositions described at page 226, Vol. II. When sulphide of potassium, made according to the first or second method, contains more than one atom of sulphur, the solution is yellow and becomes cloudy on the addition of an acid, in consequence of the deposition of sulphur. The solution evaporated out of contact of air, leaves sulphide of potassium. From a concentrated solution, absolute alcohol separates hydrated sulphide of potassium or mono-hydrosulphate of potash, in the form of an oily liquid which again redissolves in excess of alcohol. (Berzelius, *Pogg.* 6, 438.)

Sulphide of potassium unites with many electro-negative metallic sulphides, forming sulphur salts, which, when dissolved in water, may be considered as double salts of hydrosulphuric acid. It is very soluble in alcohol.

B. Double Sulphide of Hydrogen and Potassium.—*Sulph-hydrate of Potassium.*—1. When a quantity of potassium which evolves from water one measure of hydrogen gas is heated in hydrosulphuric acid gas, it takes fire and absorbs all the sulphur and half the hydrogen from two measures of the gas, leaving one measure of hydrogen free. (Gay-Lussac & Thénard.)—2. Hydrosulphuric acid gas is passed over carbonate of potash at a low red heat as long as water and carbonic acid gas—which escape with ebullition—are given off. (Berzelius.) Greyish yellow or brown (Gay-Lussac & Thénard); white (but yellowish if the access of air be not entirely prevented) crystalline and black when melted. (Berzelius.)—With dilute acids it evolves a volume of hydrosulphuric acid gas, twice as great as that of the hydrogen which the potassium present would set free from water. (Gay-Lussac & Thénard, *Recherch.* 1, 185; *Ann. Chim.* 95, 164; *Ann. Chim. Phys.* 14, 363.)

| | | Calculation. | | Or: | | Calculation. | |
|---|---|---|---|---|---|---|---|
| KS | 55·2 | | 76·46 | K | 39·2 | | 54·30 |
| HS | 17·0 | | 23·54 | 2S | 32·0 | | 44·32 |
| | | | | H | 1·0 | | 1·38 |
| KS,HS | 72·2 | | 100·00 | ,, | 72·2 | | 100·00 |

It deliquesces rapidly in the air; and when put into water forms, without effervescence, a clear solution which may be considered either as solution of double sulphide of hydrogen and potassium or as bi-hydrosulphate of potash (*zweifach hydrothion-kali*). The same liquid is obtained by saturating a solution of potash with hydrosulphuric acid in a close vessel, and boiling to expel the excess of gas retained by the water. If solution of potash be put into a tubulated retort—and, by means of a tube fitted into the neck, hydrogen gas be passed into the retort till all the air is expelled—then hydrosulphuric acid gas, as long as it is absorbed—then again hydrogen gas, while the liquid is heated till it is evaporated to the consistence of syrup—and finally the retort closed,—large colourless crystals are obtained, having the form of four and six-sided prisms, terminated by four and six-sided summits. The crystals when exposed to the air again deliquesce to a syrup. (Berzelius.) The aqueous solution smells slightly of sulphuretted hydrogen, tastes strongly alkaline and bitter, has a strong alkaline reaction, and acts corrosively on organic substances. It changes in the air—first forming a yellow solution of pentasulphide of potassium and potash, or hydrosulphite of potash and excess of potash :

$$5(KS, HS) + 8O = 2KS^5 + 3KO + 5HO;$$

or: $$5(KO, 2HS) + 8O = 2(KO, HS^5) + 3KO + 8HO.$$

and subsequently a colourless solution of hyposulphite of potash:

$$KS, HS + 4O = KO, S^2O^2 + HO;$$

or: $$KO, 2HS + 4O = KO, S^2O^2 + 2HO.$$

But at the same time the carbonic acid of the air expels some of the sulphuretted hydrogen gas—hence the odour. Sulphur, especially with the aid of heat, drives out half the hydrosulphuric acid, and dissolves, producing yellowish brown pentasulphide of potassium or hydrosulphite of potash. Acids liberate sulphuretted hydrogen gas, but do not throw down sulphur, unless the solution has been exposed to the air.

C. Bi-sulphide of Potassium.—1. One atom of bisulphate of potash is heated to redness with 7 atoms or more of charcoal. (Geiger.)—2. The alcoholic solution of the double sulphide of hydrogen and potassium is exposed to the air till a film of hyposulphite of potash begins to form on the surface, and then evaporated to dryness in a close vessel. (Berzelius.) When a mixture of 276·8 parts (4 At.) of carbonate of potash with rather less than 112 parts (7 At.) of sulphur is heated to redness, bisulphide of potassium is obtained, mixed with sulphate and undecomposed carbonate of potash.

$$4(KO, CO^2) + 7S = 3KS^2 + KO, SO^3 + 4CO^2. \quad \text{(Berzelius.)}$$

The salt prepared according to the first method is yellowish red, of crystalline texture, and deliquescent. (Geiger, *N. Tr.* 3, 1, 453.) That prepared according to the second, is orange-yellow, not crystalline, and easily fusible. (Berzelius.) The aqueous solution is yellow when exposed to the air, and passes into hyposulphite of potash without depositing sulphur. It contains either bisulphide of potassium or a mixture of hydrosulphate and hydrosulphite of potash.

$$4KS^2 + 4HO = 3(KO, HS) + KO, HS^5.$$

| | | Calculation. | |
|---|---|---|---|
| K | 39·2 | | 55·06 |
| 2S | 32 | | 44·94 |
| $K, S^2$ | 71·2 | | 100·00 |

D. TERSULPHIDE OF POTASSIUM.—1. Vapour of bisulphide of carbon is passed over carbonate of potash heated to redness, as long as a permanent gas is evolved.—2. A mixture of 276·8 parts (4 At.) of carbonate of potash and 160 parts (10 At.) of sulphur is gradually heated to redness. A mixture, which swells up from the escape of carbonic acid gas, is thus formed, containing 1 atom of sulphate of potash and 3 atoms of tersulphide of potassium.

$$4(KO, CO^2) + 10S = 3KS^3 + KO, SO^3 + 4CO^2.$$

With a smaller quantity of sulphur, the same mixture is formed, contaminated however with the excess of carbonate of potash, provided that the heat be raised by degrees merely to low redness, or till the mass is brought into a state of tranquil fusion; with a stronger heat, on the other hand, bisulphide of potassium is formed, with rapid escape of carbonic acid.

Yellowish brown when solid—black when fused. (Berzelius.) The brownish yellow solution in water becomes colourless in the air, from formation of hyposulphite of potash and deposition of one atom of sulphur. It contains either tersulphide of potassium or one atom of hydrosulphate with one atom of hydrosulphite of potash.

$$2KS^3 + 2HO = KO, HS + KO, HS^5.$$

| | | Calculation. |
|---|---|---|
| K | 39·2 | 44·96 |
| 3S | 48·0 | 55·04 |
| $KS^3$ | 87·2 | 100·00 |

Berzelius, in passing hydrosulphuric acid gas over red-hot sulphate of potash as long as water was formed (sulphur at the same time being deposited from the gas), obtained a compound which was red and transparent when cold, fused readily and then became black; dissolved in water with a yellow colour, and contained 40·45 per cent. of potassium with 59·55 of sulphur. Berzelius is inclined to regard this substance as a combination of 2 atoms of potassium with 7 atoms of sulphur, or as a $3\frac{1}{2}$-*sulphide of potassium*.

E. TETRASULPHIDE OF POTASSIUM.—1. Sulphate of potash at a red-heat is decomposed by vapour of sulphide of carbon.—2. A mixture of 3 atoms of pentasulphide of potassium and 1 atom of sulphate of potash is prepared by heating together 1 part of carbonate of potash with 2 parts of sulphur; the free sulphur is driven off; and hydrosulphuric acid gas passed through the fused mass as long as water and sulphur are set free. The hydrogen of the hydrosulphuric acid combines with the oxygen of the sulphuric acid and of the potash, whilst its sulphur is deposited in another part of the tube; and there remains $15 + 1 = 16$ atoms of sulphur with $3 + 1 = 4$ atoms of potassium $= 4 : 1$.

Yellowish brown. (Berzelius.) The brownish yellow aqueous solution of this compound, when exposed to the air, deposits 2 atoms of sulphur and is converted into hyposulphite of potash. It may be supposed to contain 1 atom of hydrosulphate of potash and 3 atoms of hydrosulphite.

$$4KS^4 + 4HO = KO, HS + 3(HO, HS^5).$$

| | Calculation. | | Berzelius. |
|---|---|---|---|
| K | 39·2 | 37·98 | 36 |
| 4S | 64·0 | 62·02 | 64 |
| $KS^4$ | 103·2 | 100·00 | 100 |

If through a mixture of tetrasulphide of potassium and excess of sulphur kept at a red-heat hydrosulphuric acid gas (or any other gas that does not cause oxidation) is passed, till sulphur ceases to be carried off by it, 2 atoms of potassium remain in combination with 9 atoms of sulphur. This compound is considered by Berzelius as a separate degree of sulphuration, which may be called $4\frac{1}{2}$-*sulphide of potassium*.

F. Pentasulphide of Potassium.—1. Potassium or one of the sulphides previously described is heated in a retort, with excess of sulphur, till the excess of sulphur is volatilized. ¶ When a mixture of potash and excess of sulphur is fused at 105°, the result is simply monosulphide of potassium mixed with hyposulphite of potash; but at a higher temperature, the latter is decomposed into pentasulphide of potassium and sulphate of potash.

$$4(KO,S^2O^2) = 3(KO,SO^3) + KS^5.$$

(Fordos and Gélis, *Ann. Chim. Phys.* 3, 18, 86.) ¶—2. Four atoms (4 . 69·2 = 276·8 parts) of carbonate of potash are gradually heated to low redness, with at least 16 atoms (16 . 16 = 256 parts) of sulphur—*e. g.* equal parts of each—(*Sch.* 37.)

$$4(KO,CO^2) + 16S = 3KS^5 + KO,SO^3 + 4CO^2.$$

The mass is very apt to swell up and pass out of the vessel; if the carbonate of potash contains moisture, hydrosulphuric acid gas is evolved together with the carbonic acid. The excess of sulphur however great is volatilized; or if the heat be but moderate, it remains in the form of a separate stratum on the top of the mixture of 3 atoms of pentasulphide of potassium and 1 atom of sulphate of potash. When carbonate of potash is heated with an equal quantity of sulphur, not beyond 250°, all the carbonic acid is equally driven away, but the residue is a mixture of pentasulphide of potassium and hyposulphite of potash. (Mitscherlich.)

$$3KO + 12S = 2KS^5 + KO,S^2O^2.$$

—3. Hydrate of potash is gently heated with excess of sulphur. A mixture is thus formed of one atom of pentasulphide of potassium and one atom of hyposulphite of potash, which rises in part above the sulphide of potassium in the form of a white salt.

$$3(KO,HO) + 12S = 2KS^5 + KO,S^2O^2 + 3HO.$$ (Berzelius.)

Dark yellowish brown, fusible, smelling of sulphuretted hydrogen, having an alkaline bitter taste, and alkaline reaction.

| | | Calculation. | |
|---|---|---|---|
| K | 39·2 | | 32·89 |
| 5S | 80·0 | | 67·11 |
| K, $S^5$ | 119·2 | | 100·00 |

Pentasulphide of potassium gives up its excess of sulphur at a red-heat to silver (as well as many other metals; *Berzelius*), so that water dissolves out protosulphide of potassium, and leaves sulphide of silver behind. (Vauquelin, *Ann. Chim. Phys.* 6, 25.) It burns, when heated in the air, producing sulphate of potash and sulphurous acid. When kept in badly closed vessels, it oxidizes gradually and forms a mixture of hyposulphite of potash and sulphur.

$$KS^5 + 3O = KO,S^2O^2 + 3S.$$

It dissolves very readily in water and alcohol, forming a yellowish brown solution; when it dissolves in water, cold is produced, according to

H. Rose (*Pogg. 55, 533*); alcohol leaves undissolved the sulphate or hyposulphite of potash which is found mixed with the salt prepared according to the second and third methods.—The aqueous solution contains either pentasulphide of potassium, or hydrosulphite of potash. ($KS^5+HO=KO,HS^5$).

A solution of the same nature is obtained in either of the following ways: 1. The aqueous solution of one of the preceding sulphides of potassium or of the double sulphide of hydrogen and potassium is digested with sulphur till saturated. When the double sulphide of hydrogen and potassium is thus treated, it gives up 1 atom of hydrosulphuric acid.—2. A solution of potash is boiled with sulphur. In this case, hyposulphite of potash is formed at the same time (*vid.* the third formula given for the pentasulphide of potassium). Carbonate of potash when boiled for a longer time behaves like caustic potash (H. Rose, *Pogg.* 17, 327). The yellowish brown solution when exposed to the air deposits 3 atoms of sulphur and is converted into hyposulphite of potash. By the gradual addition of an acid, it is resolved into a salt of potash, hydrosulphuric acid, and 4 atoms of sulphur, which is precipitated in the form of milk of sulphur; if on the contrary it is gradually added to an excess of acid—hydrochloric acid for instance—it is converted into a salt of potash and persulphide of hydrogen. The bisulphide, tersulphide, and tetrasulphide of potassium behave in the same manner, except that when treated with excess of acid, they always yield hydrosulphuric acid together with the persulphide of hydrogen. Hydrosulphuric acid passed through this solution precipitates 4 atoms of sulphur and produces bisulphide of potassium (Duflos, *Schw.* 62, 212); so that the affinities are reversed according to the temperature.—The solution gives up 4 atoms of sulphur to many of the heavy metals, and with peculiar rapidity to copper, and is thereby converted into a colourless solution of monosulphide of potassium. (Vauquelin.) When heated, it dissolves an additional quantity of sulphur; but this again separates on cooling. (Berzelius.)

*Liver of Sulphur, Hepar sulphuris salinum seu alcalinum*,—which is prepared by gently heating sulphur with carbonate of potash in closed vessels, *e. g.* in covered earthen or cast-iron crucibles,—but freest from impurity, in glass flasks,—consists of tersulphide, pentasulphide, and intermediate sulphides of potassium, according to the proportions employed, mixed with sulphate and often at the same time with carbonate of potash. By taking 276·8 parts (4 At.) of carbonate of potash, and 10.16=160 parts (10 At.) of sulphur, a mixture is obtained consisting of 1 atom of sulphate of potash and 3 atoms of tersulphide of potassium. When less sulphur is used and a lower heat applied, it likewise contains undecomposed carbonate of potash; if the heat be stronger, the tersulphide changes to the bisulphide, and a larger quantity of carbonate of potash is decomposed. Lastly, if the amount of sulphur exceeds 10 atoms, the excess converts the bisulphide into tetrasulphide or pentasulphide of potassium. 4 atoms of carbonate of potash require 16 atoms of sulphur to form pentasulphide of potassium. Consequently, for 276·8 parts of carbonate of potash, 160 parts of sulphur is the smallest quantity that can be used, and this produces tersulphide of potassium; 256 parts is the largest,—pentasulphide being produced; any excess of sulphur beyond this volatilizes without entering into combination. In the common proportion of 2 parts of carbonate of potash to 1 part of sulphur, the quantity of sulphur is therefore too small.

G. Hyposulphite of Potash.—1. By boiling sulphite of potash with sulphur. In this way, trithionate of potash is also formed under certain circumstances.—2. By exposing to the air the aqueous or alcoholic solution of the double sulphide of potassium and hydrogen or of bisulphide, tersulphide, tetrasulphide, or pentasulphide of potassium.—Kirchhoff boils 1 part of sulphur with 3 parts of carbonate of potash and adds 8 parts of lime, renewing the water; filters; neutralizes the potash in excess with sulphuric-acid (this would not be necessary if more sulphur were employed); and evaporates: the sulphate then crystallizes out first and afterwards the hyposulphite.—Berzelius puts the alcoholic solution of bisulphide or tersulphide of potassium into a bottle loosely stopped: the hyposulphite of potash then crystallizes out, and is freed from adhering sulphide by washing with alcohol.—3. Sulphurous acid gas is passed through solution of liver of sulphur, till the liquid becomes colourless; it is then filtered and evaporated.—¶ 4. By fusing equal parts of bichromate of potash and sulphur, or 100 parts of neutral chromate with 40 parts of sulphur, a mixture of sulphate and hyposulphite of potash is obtained together with insoluble sesquioxide of chromium. Döpping (*Ann. Pharm.* 44, 172, 1843) recommends the following process. A solution of monochromate of potash (one part of salt to 8 parts of water) is digested with monosulphide of potassium in a sand bath. At a temperature just above the boiling point of the liquid, the chromate of potash is decomposed, chromic oxide being separated, and hyposulphite of potash formed; the solution is filtered, boiled to precipitate any chromic oxide held in solution, and evaporated to the crystallizing point; the salt separates in colourless prismatic crystals. Or, a solution of chromate of potash is heated with a solution of liver of sulphur (prepared by fusing together equal parts of carbonate of potash and sulphur) in a sand bath, the liver of sulphur being added in small portions at a time till green sesquioxide of chromium ceases to be precipitated. The clear solution is then boiled, as in the former case, to separate any sesquioxide of chromium—filtered, and evaporated to the crystallizing point. A small quantity of sulphate of potash is deposited first; afterwards hyposulphite of potash crystallizes out of a yellow colour and in rhombic octohedrons; the mother-liquor decanted from this salt and again evaporated, deposits lighter-coloured crystals in the form of six-sided prisms with dihedral summits. When the concentration is carried too far, the liquid frequently solidifies to a brilliant mass of needles, which differ however from the octohedral salt only in containing less water.—5. Kessler (*Pogg.* 74, 274) prepares hyposulphite of potash by a modification of Döpping's process, namely by adding a hot solution of bichromate of potash in small portions at a time to a hot solution of pentasulphide of potassium, waiting each time till the precipitated sesquioxide of chromium acquires a pure green colour.

$$2KS^5 + 4(KO,2CrO^3) = 5(KO,S^2O^2) + 4Cr^2O^3 + KO.$$

By evaporating the filtered solution at a temperature of 30°, thin four-sided prisms are obtained $=3(KO,S^2O^2) + HO$. On agitating the mother liquor of these crystals, a white crystalline powder separated, which again dissolved on applying heat and adding a small quantity of water. On cooling, however, large brilliant crystals were deposited belonging to the right prismatic system. Permanent in the air. Probably composed of $3(KO,S^2O^2) + 5HO$. ¶.—Transparent, inodorous, cooling and afterwards bitter to the taste. Crystallizes in four-sided prisms (Kirchhoff).

| | Calculation. | | Rammelsberg. | Döpping. | |
|---|---|---|---|---|---|
| | | | | Octohedral salt. | Needles. |
| 3KO | 141·6 | 48·07 | 47·71 | 42·60 | 45·15 |
| $3S^2O^2$ | 144·0 | 48·88 | 49·48 | 44·22 | 46·25 |
| HO | 9·0 | 3 05 | 3·10 | 13·18 | 8·60 |
| $3(KO,S^2O^2)+HO$ | 294·6 | 100·00 | 100·29 | 100·00 | 100·00 |

The crystals analysed by Rammelsberg were dried in vacuo. This salt loses at 200° (F. 392°) 3·1 per cent. of water; and if the heat is increased, it is converted, without any loss, into a cinnabar-red mixture of 1 atom of pentasulphide of potassium and 3 atoms of sulphate of potash. ($4\dot{K}O,S^2O^2 = KS^5 + 3\dot{K}O,SO^3$). But if the salt is not completely dehydrated before the temperature is raised, a small quantity of sulphur is given off, but no sulphurous acid. (Rammelsberg, *Pogg.* 56, 296.)—12·9 grammes of the salt yield on being heated: (*a*) a gas which has a most offensive odour, like that evolved from sewers, and blackens lead-salts; (*b*) 0·04 grammes of sublimed sulphur; (*c*) 2·8 grammes of a fused brownish mass which behaves like a mixture of sulphide of potassium and sulphate of potash. (Vauquelin.)—Hyposulphite of potash deliquesces in the air. The concentrated solution forms a thin syrup. When the aqueous solution of the salt contains excess of potash, it is converted, on exposure to the air, first into sulphite and then into sulphate of potash. It dissolves certain heavy metallic oxides, as the oxides of arsenic, copper, silver and mercury. (Kirchhoff.) The salt is insoluble in alcohol.

H.—¶. Pentathionate of Potash.—$KO,S^5O^5$.—Known only in solution. Very unstable (*vid.* II., 164).

I. Tetrathionate of Potash.—$KO,S^4O^5$.—1. Prepared by the gradual addition of iodine to a concentrated solution of hyposulphite of potash till the reddish brown colour becomes permanent. The tetrathionate of potash separates completely and is dissolved in hot water; the solution is then filtered from free sulphur, and mixed with alcohol till the precipitate at first formed slowly redissolves in the liquid. On cooling, the salt separates in large crystals. (Kessler, *Pogg.* 74, 249.)—2. When tetrathionic acid is added to a concentrated solution of acetate of potash, the salt separates in a pulverulent form, in which state it is more stable than when in large crystals. ¶

K. Trithionate of Potash.—$KO,S^3O^5$.—*Preparation.*—(*Vid.* II., 167.)—¶ 2. By passing a current of sulphurous acid gas through a saturated solution of hyposulphite of potash dissolved in a mixture of 7 parts of water to 1 part of alcohol. The salt separates in a crystalline pulverulent form; this powder is redissolved in water, heated to between 50° and 60°, filtered from sulphur, and mixed with an eighth part of alcohol. On cooling, trithionate of potash is deposited in slender, four-sided, obliquely truncated prisms. (Plessy, *J. für pract. Chem.* 33, 348.) ¶. —Right rhombic prisms with dihedral summits resting on the acute lateral edges. (Prevostaye, *N. Ann. Chim. Phys.* 3, 354.) Of a saline bitter flavour, neutral to vegetable colours, unaltered in the air. 100 parts of the salt heated to redness in a close vessel, evolve 11·88 parts of sulphur, and 23·76 parts of sulphurous acid, leaving 64·36 parts of sul-

phate of potash. Its solution when boiled is resolved into sulphate and sulphite of potash and free sulphur. (Pelouze.)

$$KO,S^3O^5 = S + SO^2 + KO,SO^3.$$

(Langlois, *Ann. Pharm.* 40, 102.)

| | | Calculation. | |
|---|---|---|---|
| KO | 47·2 | | 34·91 |
| $S^3O^5$ | 88·0 | | 65·09 |
| $KO,S^3O^5$ | 135·2 | | 100·00 |

L. Sulphite of Potash.—*a.* Monosulphite. *Stahl's sulphur salt.*—Sulphurous acid gas is passed through solution of carbonate of potash in a Woulfe's apparatus, till the carbonic acid is expelled; the solution is then evaporated out of contact of air. The salt forms clear crystals which contain water, but only mechanically mixed, and, according to Bernhardi (*N. Tr.* 9, 2, 14), are identical in form with those of the simple sulphate of potash. The crystals, according to the above, are abruptly truncated, irregular, double six-sided pyramids, with a short prism often intervening (*Fig.* 76), &c. It has a penetrating, acrid, and sulphurous taste.

¶ According to Muspratt (*Ann. Pharm.* 50, 259, 1844), the salt crystallizes in oblique rhombic octohedrons, containing 2 atoms of water. ¶

| | Calculation. | | Thomson. | Muspratt. |
|---|---|---|---|---|
| KO | 47·2 | 59·59 | 54·5 | 48·51 |
| $SO^2$ | 32·0 | 40·41 | 43·5 | 32·75 |
| Water by decrepitation | | | 2·0 | 18·74 |
| $KO,SO^2$ | 79·2 | 100·00 | 100·0 | 100·00 |

Decrepitates when heated, losing, first water, then a little sulphurous acid, and then sulphur in small quantity, and leaves a reddish mixture of sulphate of potash and sulphide of potassium. (Vauquelin, *Ann. Chim. Phys.* 6, 19.)

$$4(KO,SO^2) = 3(KO,SO^3) + KS.$$

It detonates with nitre. (Bergman, *Opusc.* 3, 384.) Becomes opaque in the air, and is converted into sulphate of potash, but more rapidly when in solution. In solution it reduces the oxides of mercury, silver, and gold, to the metallic state; the higher oxides of manganese, iron, and copper, to a lower degree of oxidation; and is itself converted into sulphate of potash. The solution is decomposed by baryta or lime-water, which throws down from it sulphite of baryta or lime; likewise, by double affinity, by the phosphate, sulphate, hydrochlorate, or nitrate of ammonia or soda, as well as by soluble salts of baryta or lime. The salt dissolves in 1 part of cold, and in a smaller quantity of hot water. (Fourcroy & Vauquelin, *Ann. Chim.* 24, 254; also *Crell. Ann.* 1800, 2, 395.)

*b.* Bisulphite. ¶ Prepared by supersaturating a rather strong solution of carbonate of potash with sulphurous acid, and precipitating with absolute alcohol. A white acicular mass of crystals is obtained which must be collected on a filter and washed with absolute alcohol. The salt has an unpleasant sulphurous taste, is neutral to test paper, and slowly evolves sulphurous acid in the air. By leaving the supersaturated solution in a close vessel for some weeks, the salt is obtained in beautiful rhombic prisms. Its formula is $KO,2SO^2,HO$.

The salt may be obtained in the anhydrous state by passing sulphurous acid gas into a hot saturated solution of carbonate of potash till

effervescence ceases. The solution acquires a green colour, and deposits the compound in hard granular crystals, which must be collected on a filter, washed with a small quantity of alcohol, and dried between blotting-paper. This salt dissolves but slowly in water and alcohol, and is quite insoluble in ether. Has a saline and not unpleasant taste; does not evolve sulphurous acid in the air. When it is heated in a tube, sulphur sublimes and large quantities of sulphurous acid are evolved, sulphate of potash being left behind.

$$2(KO,2SO^3) = SO^2 + S + 2(KO,SO^3).$$

(Muspratt, *Ann. Pharm.* 50, 259.) ¶ Crystallizes more easily than the neutral sulphite; gives off one-half its acid when boiled with sulphur and water. (Berzelius, *Lehrb.* 3, 81.)

M. Hyposulphate of Potash.—Hyposulphate of lime is precipitated at a boiling heat by carbonate of potash, or hyposulphate of baryta by sulphate of potash, at common temperatures, or hyposulphate of manganese by potash, always in equivalent proportions; the solution is filtered and evaporated. The crystals are transparent and belong to the right prismatic system (*Fig.* 77), without the *t* surface and the surface situated above it, having on the contrary the *p* surface; $u^1 : u = 119° 54'$; $p : a = 126° 39'$. (It has the crystalline form of sulphate of potash; Walchner, *Schw.* 44, 245.) The crystals have a pure bitter taste, and are unacted on in the air; decrepitate strongly with heat; and leave 72·49 per cent. of sulphate of potash. They dissolve in 16·5 parts of water at 16° (60·8° F.), in 1·58 parts of boiling water, but not in alcohol. (Heeren, *Pogg.* 7, 72.)

| | Crystallized. | | | | Heeren. |
|---|---|---|---|---|---|
| KO | 47·2 | ..... | 39·60 | ..... | 39·86 |
| $S^2O^5$ | 72·0 | ..... | 60·40 | ..... | 58·75 |
| Water of decrepitation | | ..... | | ..... | 1·39 |
| $HO,S^2O^5$ | 119·2 | ..... | 100·00 | ..... | 100·00 |

N. Sulphate of Potash.—*a.* Monosulphate.—*Vitriolized tartar, Tartarus vitriolatus, Arcanum duplicatum, Sal polychrestum Glaseri, Sal de duobus, Specificum purgans Paracelsi, Panacæa holsatica, Panacæa duplicata, Nitrum vitriolatum, Spiritus vitrioli coagulabilis.*—Hydrate of potash sprinkled with oil of vitriol emits light in the dark (Heinrich); it also absorbs the vapour of anhydrous sulphuric acid at ordinary temperatures. (H. Rose.)—The salt is obtained as a by-product in the preparation of nitric acid and English oil of vitriol, and in the purification of crude potash. Crystals clear, hard, and generally small. Specific gravity = 2·6232 (Karsten), = 2·636 (Watson), = 2·662 (Kopp). Crystalline system, the right prismatic (*Fig.* 76 & 77). $u^1 : u = 73° 28\frac{3}{4}'$; $u : m = 126° 44\frac{1}{2}'$; $u : t = 143° 15\frac{3}{5}'$; $n : n = 112° 22'$; $n : m = 146° 11'$; $n : t = 123° 49'$; $p : y = 150° 12'$; $y : m = 119° 48$; $y : y$ below $= 120° 24'$; $p : a = 136° 14\frac{1}{2}'$; $a : u = 133° 45\frac{1}{2}'$. (Mitscherlich, *Pogg.* 18, 169; see also the differing statements of Brooke, *Ann. Phil.* 23, 20; W. Phillips, *Ann. Phil.* 20, 342; and Bernhardi, *N. Tr.* 9, 2, 14.) Decrepitates in the fire, and fuses at a red heat; crystallizes as it becomes solid. Not volatile; tastes feebly saline and bitter.

| | Crystallized. | | Wenzel. | Kirwan. | Dalton. | Berard. | Curaudau. | Thenard & Roard. |
|---|---|---|---|---|---|---|---|---|
| KO | 47·2 | 54·13 | 54·75 | 55 | 55·3 | 57·24 | 57·71 | 63·6 |
| $SO^3$ | 40·0 | 45·87 | 45·25 | 45 | 44·7 | 42·76 | 42·29 | 36·4 |
| $KO,SO^3$ | 87·2 | 100·00 | 100·00 | 100 | 100·0 | 100·00 | 100·00 | 100·0 |

| | Bucholz. | Thomson. |
|---|---|---|
| KO | 55·67 | 67·6 |
| $SO^3$ | 43·33 | 31·0 |
| HO | 1·00 | 1·4 |
| | 100·00 | 100·0 |

Heated to redness with $\frac{1}{3}$ its weight of charcoal, it is changed into protosulphide of potassium. Most of the stronger acids separate half of its potash, and leave bisulphate of potash (I., 126, and *Sch.* 88). 2 atoms of sulphate of potash dissolved in 1 atom of moderately warm hydrochloric acid, yield, on cooling, tabular crystals of bisulphate of potash and cubes of chlorine of potassium; from bisulphate of potash, on the contrary, hydrochloric acid cannot abstract potash. (Kane, *Ann. Pharm.* 19, 1.) The powdered salt absorbs the vapour of anhydrous sulphuric acid very slowly and gives it off entirely on being warmed. (H. Rose, *Pogg.* 38, 122.)—100 parts of water at 0° dissolve, with slight lowering of temperature, 8·36 parts of the salt, and for every degree above 0°, 0·1741 parts. (Gay-Lussac.) A solution saturated at 8° has a specific gravity of 1·072. (Anthon, *Repert.* 59, 346)—1 part of sulphate of potash dissolves in 9·3 parts of water at 18·75°, and the solution has a specific gravity = 1·0798. (Karsten.) In solution of potash of 1·35 specific gravity, it is quite insoluble. (Liebig, *Ann. Pharm.* 11, 262; also Brandes & Firnhaber, *Berl. Jahrb.* 24, 2, 68; and Brandes & Gruner, *Br. Arch.* 22, 147.)

*b.* Sesqui-sulphate.—Crystallizes from a solution of the normal sulphate in dilute sulphuric acid, together with bisulphate of potash, and in the form of asbestos-like threads. (R. Phillips, *Phil. Mag. Ann.* 1, 429; also *Kastn. Arch.* 13, 198.) Jacquelain succeeded but once in obtaining this salt.

| | Crystallized. | | Phillips. |
|---|---|---|---|
| 2KO | 94·4 | 42·26 | 42·80 |
| $3SO^3$ | 120·0 | 53·71 | 52·45 |
| HO | 9·0 | 4·03 | 4·75 |
| $2(KO, SO^3) + HO, SO^3$ | 223·4 | 100·00 | 100·00 |

*c.* Bisulphate.—1. 87·2 parts (1 At.) of sulphate of potash are melted together with 49 parts (1 At.) of oil of vitriol.—2. A hot solution of 1 atom of sulphate of potash in a mixture of $\frac{1}{2}$....1 atom of vitriol and water, yields crystals of the normal salt immediately on cooling; the mother-liquor drawn off and evaporated, afterwards yields needles of the anhydrous bi-acid salt. These may also be obtained by evaporating a solution of 1 atom of sulphate of potash in $1\frac{1}{2}$....2 atoms of sulphuric acid; but the mass of salt obtained by evaporation in the latter case, liquefies in the course of 5 days, and yields rhombohedrons of the hydrated bi-acid salt; with 3 atoms of sulphuric acid to one of sulphate of potash, this change occurs sooner; and with 5 atoms, even in one hour. Both the anhydrous and the hydrated salt can be formed as well at common temperatures as at 40°; the former especially when the sulphuric acid is present in small quantity, and the latter when it is in excess. From a solution of 1 atom of sulphate of potash and 1 atom of oil of vitriol in hot hydrated hydrochloric, nitric, tartaric, or acetic acid, only the hydrated rhombohedral salt crystallizes out, so that these acids act in the same manner as an excess of sulphuric acid. (Jacquelain.) When the residue left after the preparation of nitric acid from 1 atom of nitre and 2 atoms of sulphuric acid is dissolved in hot water and cooled, sulphate of

potash first separates in crystals, which have a sour taste, but only in consequence of the solution still adhering to them; and the mother-liquor, on being afterwards placed in a cool situation, yields needles, and at last short thick prisms of the hydrated biacid salt, whilst a large portion solidifies in a dendritic mass of minute crystals. (Geiger.)—The anhydrous salt crystallizes in fine needles, having a specific gravity of 2·277, and melting at 210° (410° F.). Dissolved only in the exact quantity of hot water necessary, it crystallizes unaltered on cooling; but when this mass is exposed to the air for 4 weeks, the hydrated salt separates from it in a mass of small needles. (Jacquelain.)

The hydrated salt crystallizes partly ($\alpha$) in rhombohedrons, having a specific gravity of 2·163, and fusing at 197° (386·6 F.), partly ($\beta$) on separating from the anhydrous salt, in shining silky threads, produced from the union of the rhomboids. (Jacquelain.)—The hydrated salt which separates in larger crystals from the aqueous solution is isomorphous with the oblique prismatic sulphur; but on cooling after fusion, crystals are produced identical with those of felspar; the salt is consequently dimorphous. (Mitscherlich.) It sometimes crystallizes in transparent, thick, oblique, rhomboidal prisms, $\alpha$, with numerous truncations; sometimes in four or six-sided needles, $\beta$. (Geiger.)—Beudant (*Ann. Chim. Phys.* 4, 72) obtained from a solution of sulphate of potash in oil of vitriol, irregular tetrahedrons; from a solution in weaker acid, rhombohedrons; and in acid still more diluted, rhombohedrons with P-faces and other faces likewise. Phillips obtained right rhombic prisms and rhombic octohedrons.—The hydrated crystals retain their transparency at 149° (300·2° F.), and first begin to melt at 315·5° (600° F.), when they merely lose a trace of mechanically combined water. (Graham.) They fuse at 200° (392° F.). (Mitscherlich.) The fused salt appears as a pellucid oil, and solidifies on cooling to a white transparent hard mass. It tastes very sour, and reddens litmus strongly.

| | Anhydrous. | | Jacquelain. |
|---|---|---|---|
| KO | 47·2 | 37·11 | 37·05 |
| $2SO^3$ | 80·0 | 62·89 | 62·95 |
| $KO, 2SO^3$ | 127·2 | 100·00 | 100·00 |

| | Hydrated. | | Jacquelain. | | Geiger. | |
|---|---|---|---|---|---|---|
| | | | $\alpha$ | $\beta$ | $\alpha$ | $\beta$ |
| KO | 47·2 | 34·65 | 34·55 | 34·56 | 32·53 | 33·83 |
| $2SO^3$ | 80·0 | 58·74 | 58·48 | 58·69 | 54·77 | 55·43 |
| HO | 9·0 | 6·61 | 6·97 | 6·75 | 12·70 | 10·74 |
| | 136·2 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

The hydrated salt is considered by Graham and others as a double salt, water being one of the bases; thus, $KO, SO^3 + HO, SO^3$. The hydrated salt is not decomposed below a red heat; according to Gay-Lussac, it gives off when heated to redness, first oil of vitriol, then sulphurous acid and oxygen gas, and is converted into the normal salt. Anhydrous sulphate of magnesia or sulphate of zinc expels oil of vitriol from the salt when in a state of fusion, and unites in its stead with the simple sulphate of potash to form a double salt. $KO, SO^3 + HO, SO^3$ with $MgO, SO^3$; yields $KO, SO^3 + MgO, SO^3$, and $HO, SO^3$. (Graham.) Fused common salt mixed with the hydrated salt in the fused state, immediately evolves hydrochloric acid. (Mitscherlich.)

Bisulphate of potash dissolves in about half its weight of boiling water; the solution solidifies to a mass of needles on cooling. From a

solution in a larger quantity of hot water a considerable quantity of simple sulphate crystallizes out on cooling, leaving free acid in the solution, and this in proportion to the amount of water employed (up to a certain limit). (Geiger.) When much water is present, the addition of even a large quantity of sulphuric acid cannot prevent the simple sulphate from crystallizing out. (Graham.) When the water is in large excess, its affinity for the sulphuric acid overcomes that of the sulphate of potash for the latter. Cold water extracts from the salt a large quantity of sulphuric acid and but little potash, leaving simple sulphate of potash; the prismatic crystals are therefore deprived of their transparency by cold water. Boiling alcohol also extracts from the crystals scarcely anything but sulphuric acid, and leaves them cloudy and less acid to the taste. (Geiger; also Link, *Crell. Ann.* 1796, 1, 26; Berthollet, *Stat. Chim.* 1, 356; Geiger, *Mag. Pharm.* 9, 251; R. Phillips, *Phil. Mag. Ann.* 1, 429, and *Kastn. Arch.* 13, 198; Mitscherlich, *Pogg.* 18, 152....173; Graham, *Phil. Mag. J.* 6, 331; Jacquelain, *Ann. Chim. Phys.* 70, 311.)

According to Jacquelain, there exist crystalline compounds of simple sulphate of potash with hydrated phosphoric and nitric acids. If simple sulphate of potash is dissolved in excess of warm *syrupy phosphoric acid*, oblique six-sided prisms are obtained on cooling, having a specific gravity = 2·296, melting at 240° (464° F.), and containing 63·6 per cent. of sulphate of potash, 26·35 of phosphoric acid, and 10·5 of water = $2(KO,SO^3) + 3HO,PO^5$. A solution of sulphate of potash in warm *nitric acid* yields, first a few crystals of hydrated bisulphate of potash and nitre—then oblique prisms, of specific gravity 2·381, which fuse at 150° (302° F.), and consist of 39·32 per cent. of potash, 33·29 of sulphuric acid, and 27·47 of the first hydrate of nitric acid = $2(KO,SO^3) + HO,NO^5$. When dissolved, on the contrary, in hydrochloric or tartaric acid, it yields hydrated bisulphate of potash on the one hand, and chloride of potassium or cream of tartar on the other.

The above two compounds, however, may likewise be regarded as combinations of hydrated bisulphate of potash with phosphate or nitrate of potash:

$$2(KO,SO^3) + 3HO,PO^5 = KO,HO,2SO^3 + KO,2HO,PO^5;$$

and: $2(KO,SO^3) + HO,NO^5 = KO,HO,2SO^3 + KO,NO^5$.

O. Double Sulphide of Carbon and Potassium.—In the state of solution it may also be considered as *hydrosulphuretted carbonate of potash*.—1. Formed by dissolving sulphide of carbon in a solution of protosulphide of potassium, or of potash; in the latter case, slowly, and with production of carbonate of potash at the same time.—To a solution of protosulphide of potassium in a small quantity of alcohol, sulphide of carbon is added as long as it dissolves, the lower syrupy stratum which separates on standing, is separated from the two upper ones (the middle stratum being the excess of sulphide of carbon—and the upper one, alcohol holding in solution higher sulphides of potassium and sulphide of carbon), and evaporated at 30° (86° F.).—2. An aqueous solution of protosulphide of potassium is digested to saturation with excess of sulphide of carbon, at 30° (86° F.), in a closed vessel quite filled with the mixture, and then evaporated at the same temperature.—In both cases, a yellow, highly deliquescent salt crystallizes from the concentrated solution, having a cooling, peppery, and afterwards hepatic taste; it loses its water of crystallization at a temperature between 60° and 80° (140° and 176° F.), and is converted into anhydrous double sulphide of carbon and potassium. This substance

is reddish brown, and when heated apart from the air, changes without any separation of liquid matter, to a blackish-brown mixture of tersulphide of potassium and charcoal.

$$KS, CS^2 = KS^3 + C.$$

It readily dissolves in water, but is very sparingly soluble in alcohol, forming a brown solution. (Berzelius, *Pogg.* 6, 450.)

P. Sulphophosphide of Potassium.—Dry spontaneously inflammable phosphuretted hydrogen gas is passed for 7 hours over gently heated 3½-sulphide of potassium (p. 33). Hydrosulphuric acid gas is evolved, and a white mass obtained, having a hepatic taste.

$$4K, 14S + PH^3 = 4KS^2, PS^3 + 3HS.$$

| | Calculation. | | H. Rose. |
|---|---|---|---|
| 4K | 156·8 | 43·05 | 42·32 |
| 11S | 176·0 | 48·33 | 45·02 |
| P | 31·4 | 8·62 | |
| $4KS^2, PS^3$ | 364·2 | 100·00 | |

In the determination of the sulphur by oxidation with nitric acid, Rose sustained a loss, owing to the escape of sulphuretted hydrogen.

The mass deliquesces in the air and dissolves completely in water, giving out the odour of hydrosulphuric acid; if hot water is used, the gas escapes in bubbles, and phosphoric acid is produced at the same time. The solution mixed with hydrochloric acid, evolves hydrosulphuric acid gas and deposits sulphur. After this, it probably contains one atom of triphosphate of potash, one atom of tersulphide of potassium, and 8 atoms of hydrosulphuric acid.

$$4KS^2 + PS^3 + 8HO = 3KO, PO^5 + KS^3 + 8HS. \quad \text{(H. Rose.)}$$

*b.* When sulphide of hydrogen and potassium is treated in the same manner with phosphuretted hydrogen gas, it is converted, with evolution of sulphuretted hydrogen, (which escapes with great frothing) into a semi-fluid mass, which, on cooling, acquires a very faint yellowish red tinge, contains more potassium and phosphorus than the preceding, and absorbs moisture from the air with avidity. (H. Rose, *Pogg.* 24, 313.)

## Potassium and Selenium.

A. Selenide of Potassium.—1. Formed by direct combination of selenium with potassium. The combination is attended with inflammation, by which a portion of the selenide becomes sublimed; and when there is an excess of potassium present, with a kind of explosion.—2. By igniting selenite or seleniate of potash, with hydrogen gas or charcoal.—3. By fusing selenium with hydrate of potash, by which a mixture is formed of 2 atoms of selenide of potassium and 1 atom of selenite of potash.

$$3KO + 1Se + xSe = 2KSe^x + KO, SeO^2;$$

The amount of selenium with which the potassium combines, is not here inquired into).—4. By heating selenium with carbonate of potash, whereby the carbonic acid is expelled, and the same effects produced as in the third method. The selenide of potassium obtained by the first method, is

a fused steel-grey mass, having a crystalline fracture, and a taste and smell like liver of sulphur. That prepared by the second method is dark brown on the surface, but cinnabar-red within. That prepared by the third method is black in the mass, but brown when pulverised; spongy, infusible at a red-heat, and richer in selenium than the preceding. The selenide of potassium which contains selenium in excess, swells up when hydrochloric acid is poured over it, evolves seleniuretted hydrogen, and deposits red flakes of selenium.

Selenide of potassium becomes moist in the air. When it contains excess of potassium, it dissolves in water with evolution of hydrogen gas, and produces a pale red solution (probably colourless, however, when the presence of oxygen is entirely prevented), in which hydrated protoselenide of potassium or *hydroseleniate of potash*, must be supposed to exist.—The selenide richer in selenium, obtained by the first and third methods, yields, with water, a dark reddish brown solution, from which acids liberate seleniuretted hydrogen and precipitate selenium. In the solution, a hydrated perselenide of potassium, or *hydroselenite of potash* must be supposed to exist. A similar solution, though likewise containing selenite of potash, is formed by boiling selenium for a long time in solution of potash. The selenide of potassium still richer in selenium, obtained by the fourth method, forms with a small quantity of water, a dark brown solution, from which, on the addition of more water, the greater part of the selenium is thrown down, (unless undecomposed carbonate of potash is present, which prevents the precipitation), and the same reddish brown liquid remains as in the former case. All the solutions of selenide of potassium have a hepatic taste, and when exposed to the air, deposit selenium in the form of a red powder.

$KSe^x + O = KO + Se^x$; or, $KO,HSe^x + O = KO + Se^x + HO$. (Berzelius.)

B. Selenite of Potash.—*a. Monoselenite.*—Obtained by saturating carbonate of potash with selenious acid. On evaporating the solution, but not by cooling, it separates in crystalline grains. Fuses, when heated, to a yellow mass, which again becomes white on cooling. Attracts moisture from the air; soluble in nearly all proportions in water, but not in alcohol. Has a disagreeable taste, and strong alkaline action on test paper.

*b. Biselenite.*—Crystallizes with difficulty on cooling, from a solution evaporated to the consistence of syrup, or from a slightly acid solution by evaporation over oil of vitriol, in feathery (satiny-looking; *Muspratt*) crystals, which unite at last to a compact mass.—Slowly parts with the half of its acid when ignited.—Deliquescent, but slightly soluble in alchol. Analogous to bisulphite of potash.

*c. Quadroselenite.*—Not crystallizable, highly deliquescent. (Berzelius.)

| | Selenite. | | Muspratt. |
|---|---|---|---|
| KO | 47·2 | 45·74 | 45·02 |
| $SeO^2$ | 56 | 54·26 | |
| $KO,SeO^2$ | 103·2 | 100·00 | |

| | Bi-selenite. | | Muspratt. |
|---|---|---|---|
| KO | 47·2 | 29·65 | 28·05 |
| $2SeO^2$ | 112·0 | 70·35 | |
| $KO,2SeO^2$ | 159·2 | 100·00 | |

| | Quadroselenite. | |
|---|---|---|
| KO | 47·2 | 17·41 |
| $4SeO^2$ | 224·0 | 82·59 |
| $KO,4SeO^2$ | 271·2 | 100·00 |

C. SELENIATE OF POTASH.—*a. Monoseleniate.*—1. When selenious acid is fused with nitre, and the mass dissolved in water and evaporated, nitre crystallizes out first, and then seleniate of potash.—2. A mixture of native selenide of lead with an equal quantity of nitre, is thrown into a red-hot crucible, dissolved in hot water, filtered, and left to crystallize. The salt which crystallizes out after the nitre, is adulterated with more or less of sulphate of potash. The seleniate of potash has the exact form and optical properties of the sulphate of potash. (*Fig.* 76 and 77), $n : n = 112° 48\frac{1}{2}'$; $y : y$, below $= 120° 25'$.—It detonates on burning charcoal like nitre, and dissolves almost as readily in cold as in hot water. Mitscherlich, *Pogg.* 9, 623.)

| | Crystallized. | | Mitscherlich. |
|---|---|---|---|
| KO ..... | 47·2 ..... | 42·45 ..... | 42·16 |
| $SeO^3$ ..... | 64·0 ..... | 57·55 ..... | 57·84 |
| $KO, SeO^3$ ..... | 111·2 ..... | 100·00 ..... | 100·00 |

## POTASSIUM AND IODINE.

A. IODIDE OF POTASSIUM.—Potassium unites both with solid iodine (under slight pressure even in the cold) and also with its vapor, evolving heat, and burning with a violet flame. Iodine and potassium heated together in very small quantities unite, the combination often being attended with a powerful explosion, and breaking the glass-tube. (Sementini, *Schw.* 41, 164, Gmelin.)—Vapour of iodine separates oxygen from potash at a red heat, producing iodide of potassium.

*Preparation.*—1. Antimonide of potassium free from arsenic, prepared by fusing crystallized tartar-emetic previously roasted, is thrown in powder into a solution of one part of iodine dissolved in 12 parts of alcohol, till the colour disappears; the liquid is then filtered and evaporated till crystallization commences. The antimony remaining on the filter in powder, may be again converted into antimonide of potassium by fusing with cream of tartar, and so made use of many times. (Serullas, *Ann. Chim. Phys.* 20, 163.)

2. Pure potash or the carbonate, is saturated with hydriodic acid in solution (prepared according to method 2, II., 262), and evaporated. (Le Royer & Dumas, *Gilb.* 68, 241.)—Strating (*Repert.* 15, 288) dissolves 10 parts of iodine in 160 parts of alcohol; passes sulphuretted hydrogen through the solution till the colour disappears; then filters; distils off the greater part of the alcohol; dilutes the remainder with 132 parts of water, distils the rest of the alcohol away; saturates the solution of hydriodic acid with 11 parts of carbonate of potash; and evaporates till crystallization commences.

3. A solution of iodide of zinc, or hydriodate of oxide of zinc, is prepared by mixing zinc, iodine, and water,—precipitated by the exact amount of carbonate of potash required,—filtered, and evaporated. (Le Royer & Dumas.)—Girault gradually pours the cold filtered solution of iodide of zinc into a boiling solution of carbonate of potash till it no longer causes effervescence—adds cold water to the mixture—filters and exhausts the residue twice with cold water, (which retains only a trace of iodine in the form of oxyiodide of zinc, separable by a red heat)—precipitates the zinc still remaining in solution, by the cautious addition

of more carbonate of potash—then filters and evaporates. According to E. Hermann and Fr. Wendt, also, the precipitated carbonate of zinc obstinately retains a portion of iodine. (*Repert.* 44, 117, and 122.)

4. A solution of protiodide of iron or hydriodate of protoxide of iron is prepared from 2 parts of iodine, 1 part of iron-filings, and 10 parts of water, and filtered as soon as it becomes colourless; the protoxide of iron is precipitated by caustic potash or carbonate of potash, added in equivalent proportion, at a boiling heat, and the liquid filtered and evaporated. (Baup. *J. Pharm.* 9, 37, and 122; also *N. Tr.* 8, 2, 176; also *Repert.* 13, 237; 14, 409; Caillot, *J. Pharm.* 8, 473.) Schindler (*Mag. Pharm.* 23, 100) gradually adds 4 parts of iodine to 1 part of iron filings diffused through 20 parts of water, to prevent any iodine from volatilizing by the heat produced,—decomposes the solution with potash as soon as it becomes colourless (before any basic hydriodate of peroxide of iron is precipitated, which can be decomposed only by excess of potash), and washes the precipitate of hydrated protoxide of iron in a bottle broken off at the bottom, and tied round with paper and linen, continuing the washing uninterruptedly. The solution of iodide of iron may likewise be prepared in a cast-iron vessel. It may also be precipitated with a slight excess of potash, and exposed to the air, till the hydrated protoxide changes into the hydrated peroxide, which can be more readily washed [but probably retains iodine]. (N. E. Henry, *J. Pharm.* 13, 406.) Perhaps the best method would be to precipitate the iodide of iron by caustic potash at a boiling heat.)

5. An intimate mixture of 2 parts of powdered antimony and 5 parts of iodine is heated very gently in a glass flask, whereupon a sudden union takes place. The flask is broken after cooling, and the iodide of antimony thrown in powder into hot water, which extracts $\frac{2}{3}$ of the iodine in the form of pure hydriodic acid. The liquid is then decanted; the remaining oxyiodide of antimony digested with excess of carbonate of potash, which withdraws all the iodine; the solution filtered; and the alkaline filtrate neutralized with the hydriodic acid previously obtained. (Serullas, *J. Pharm.* 14, 19, and 25.)

6. A mixture of 2 parts of iodine, 1 part of hydrate of potash, and 6 parts of water is evaporated to dryness, and the mass heated in a retort as long as oxygen gas is given off. The iodine is then dissolved in water; the potash still remaining free, saturated with an aqueous solution of hydriodic acid; and the solution evaporated to a small bulk. (Le Royer & Dumas.) By dissolving iodine in solution of potash, iodide of potassium and iodate of potash are formed; at a red heat, the latter evolves oxygen gas, and is converted into iodide of potassium. The potash must be as free as possible from carbonate; for this salt passes into the state of bicarbonate of potash, which does not combine with the iodine, and remains as simple carbonate in the mass after it has been heated to redness. Since carbonic acid is reabsorbed during the evaporation of the caustic liquid in the preparation of hydrate of potash, good caustic solution is preferable to the solid hydrate. Into this solution, either cold or gently warmed, iodine is introduced till the liquid begins to acquire a brown tint; a larger quantity of iodine would be again driven off by subsequent heating. (Schindler, *Mag. Pharm.* 23, 100; 25, 55; Reimann, *Mag. Pharm.* 23, 89.) The heat is applied in glass retorts or flasks, or in covered porcelain or cast iron vessels, which are at most but half filled. Loss may be sustained through the splashing of the mass; and that which has fallen on the colder sides of

the vessel may contain iodate of potash undecomposed. The heat should be gentle but long continued; if, however, it be too low, iodate of potash remains undecomposed; and if too powerful, iodide of potassium volatilizes, especially when the operation is conducted in open vessels. Part of the iodine may also be expelled by heat from the iodate of potash. Hence the method discovered and recommended by Orfila, and approved of by Girault (*J. Pharm.* 27, 393), namely, to heat the dried mass, after mixing it with charcoal-powder, appears to be the most advantageous. By this means carbonic acid only is set free without any iodine, and the decomposition of the iodate of potash takes place at a much lower temperature and more rapidly. The heated mass is exhausted by water or alcohol (which leaves behind the greater part of the carbonate of potash nearly always present), and then purified by crystallization.

7. Iodine is dissolved in a warm solution of potash till a brownish colour is produced, and reddened litmus paper is no longer turned blue by it. Water is then added, and sulphuretted hydrogen passed through till the whole of the iodate is converted into iodide, and the liquid smells permanently of sulphuretted hydrogen. It is then filtered and boiled to expel the gas; potash added if the solution contains free hydriodic acid,—or solution of hydriodic acid if the potash is in excess,—and the liquid then evaporated. (Turner, *Edinb. Med. J. Nr.* 84, 20.) The sulphur precipitated in this process contains iodine; the iodide obtained is yellow even after fusion, and appears to contain sulphide as well as iodide of potassium. (Schindler.)

8. An alcoholic solution of iodine (or iodine diffused in water) is digested with an aqueous or alcoholic solution of sulphide of potassium, till the former is rendered colourless: the liquid is then filtered and evaporated. (Taddei, *J. Pharm.* 10, 179.)

$$KS^x + I = KI + S^x; \quad \text{or,} \quad KO,HS^x + I = KO,HI + S^x.$$

Taddei dissolves the iodine in alcohol of 20°—25° Bm., and adds thereto an aqueous solution of protosulphide of potassium. But the iodide of potassium thus obtained has a brown colour, arising from the use of alcohol. It is better, therefore, to diffuse 1 part of iodine in 6 parts of water, and add an aqueous solution of protosulphide of potassium, stirring constantly till the liquid becomes clear and colourless. If too much sulphide is used, the liquid becomes cloudy, and a little iodine must then be added. (Fran. *J. Pharm.* 11, 403.) Duflos (*Berl. Jahrb.* 28, 2, 211) proceeds in a similar manner, by heating 4 parts of sulphate of potash in an earthen crucible, till gentle fusion takes place; dissolving the sulphide of potassium thus obtained in 3 times its weight of water, access of air being prevented; adding iodine to the solution, till a filtered specimen appears colourless; filtering, and leaving the solution to crystallize; evaporating the mother-liquor, and igniting the residue; and afterwards digesting it in water to obtain more crystals. Even when the use of alcohol is avoided, sulphur is still found mixed with the iodide of potassium; the mass turns grey when heated, and evolves sulphuretted hydrogen—a black substance remaining mixed with it, which seems to be carbon containing sulphur. The sulphide of potassium, also, obtained by heating sulphate of potash with charcoal, may contain caustic potash and carbonate of potash, and thereby give rise to the admixture of iodate and carbonate of potash. (Schindler.) Brandes and Schrader (*Br. Arch.* 16, 103) make use of an alcoholic solution of ordinary liver of sulphur.

9. Sulphide of barium in solution is converted into iodide of barium

by means of iodine, and the filtrate precipitated by a suitable salt of potash. Liebig (*N. Tr.* 18, 2, 259) heats to redness 6 parts of heavy spar with one part of lamp-black, dissolves the sulphide of barium in water, adds iodine as long as it is dissolved, filters from the sulphur, precipitates the colourless fluid with carbonate of potash, filters again, and evaporates. Wittstock (*Pogg.* 55, 428) uses sulphate of potash. The sulphide of barium must be treated with water in sufficient quantity to dissolve the whole immediately, or else a portion of baryta will remain undissolved; and the liquid, which contains bisulphide of barium, yields with iodine more hydriodic acid than is necessary for saturating the baryta, so that an acid liquid is formed. (H. Rose.) This is prejudicial when sulphate, but not when carbonate of potash is made use of in precipitating the solution.

The carbonate of potash present in most of the specimens of iodide of potassium prepared by these methods may be removed either by neutralizing with solution of hydriodic acid, or by dissolving the iodide in alcohol.

The second, fourth, and sixth methods (if in the last, the residue is heated to redness with charcoal) are the best.

*Impurities in Iodide of Potassium.—Carbonate of potash* causes it to have an alkaline reaction, and a greater tendency to deliquesce, and gives rise to effervescence on the addition of acids; left undissolved on treating the iodide with strong alcohol.—*Iodate of potash:* the solution turns brown on the addition of hydrochloric or tartaric acid, from separation of iodine or formation of hydriodite of potash.—*Chloride of potassium or sodium:* From the precipitate which the solution gives with nitrate of silver, the chloride of silver is dissolved by excess of ammonia, and again thrown down from the filtrate by pure nitric acid. [*Vid.* Robiquet's more detailed method: *J. Pharm.* 8, 140.] *Sulphate of potash;* Precipitated by salts of baryta; left undissolved by alcohol. *Organic matter containing sulphur:* probably xanthonate of potash; becomes mixed with the iodide of potassium when alcohol, together with sulphuretted hydrogen or a metallic sulphide is used in the preparation Iodide of potassium of this kind has a nauseous taste, like that of asafœtida, turns greyish brown on being heated, and evolves sulphurous acid; the residue treated with water, leaves charcoal containing sulphur, and sulphate of potash is found in the solution, together with the iodide. (Schindler.) *Sulphide of potassium:* Evolves hydrosulphuric acid on the addition of sulphuric acid. (Marchand, *Ann. Pharm.* 66, 237.)

Iodide of potassium should dissolve entirely at ordinary temperatures, in $\frac{3}{4}$ of its weight of water, or 6 parts of alcohol of specific gravity 0·85. (Baup.) One atom (165·2 parts) of iodide of potassium completely precipitates one atom (136·8 parts) of chloride of mercury from an aqueous solution

$$KI + HgCl = KCl + HgI;$$

but the insoluble iodide of mercury again dissolves completely in one atom of iodide of potassium,

$$2KI + HgCl = KCl + KI,HgI.$$

2 atoms (330·4 parts) of the iodide of potassium to be tested, and one atom of corrosive sublimate must therefore be dissolved in two equal quantities of water. To one measure of the solution of iodide of potassium, the solution of corrosive sublimate is then to be added, till a permanent precipitate begins to appear; if one measure of the latter solution is required for this purpose, the iodide of potassium is quite pure; but if a

permanent precipitate remains when only half a measure of the corrosive sublimate has been added, the iodide of potassium is adulterated one-half with foreign substances, &c. &c. (Maroseau, *J. Pharm.* 18, 302.) Iodide of potassium separates from an aqueous solution in white crystals, sometimes transparent, sometimes semi-opaque, and having the form of cubes, elongated cubes, pyramids, or octohedrons. Kane (*Phil. Mag. J.* 16, 222) obtained crystals which appeared to belong to the square prismatic system. (*Fig.* 29 and 32); $e$ : lateral edge = 150°; $e : p = 120°$; $e : e^1 = 105°$; $e$ over the vertex : $e$ behind = 60°; it is therefore probably dimorphous; the crystals, however, exhibited simple refraction. Specific gravity = 2·9084 (Karsten), = 3·091 (Boullay). After fusion it is reduced to a crystalline mass, having a pearly lustre. (Gay-Lussac, *Gilb.* 49, 26.) It melts below a red heat; and when exposed to the air volatilizes undecomposed at a moderate red heat; if the experiment is made in a glass tube, the volatilization does not take place till the glass begins to soften. (Schindler.) It has a sharp taste, and turns reddened litmus paper slightly blue.

According to Gay-Lussac.

| | | | |
|---|---|---|---|
| K | 39·2 | | 23·73 |
| I | 126·0 | | 76·27 |
| KI | 165·2 | | 100·00 |

Chlorine, with the aid of heat, converts iodide of potassium into chloride of potassium and iodine. (Gay-Lussac.) From a solution in 2 parts of water, chlorine gas throws down iodine at first; but this disappears again when more chlorine is added, a compound of terchloride of iodine with chloride of potassium being formed, which colours the liquid yellow, and yields an abundant crop of crystals. (Filhol.)

$$KI + 4Cl = KCl, ICl^3.$$

Iodide of potassium on being evaporated with nitric acid, is wholly converted into nitrate of potash. (Serullas.) When it is heated with nitrate of ammonia, iodine is abundantly evolved with production of a brown colour. (Emmet.) Fused with chlorate of potash, it is converted into iodate of potash; heated with nitrate of potash or nitrate of baryta, it yields a small quantity of iodate of potash or baryta, together with peroxide of barium in somewhat larger quantity. (O. Henry, *J. Pharm.* 18, 345.) In the vapour of anhydrous sulphuric acid, it turns reddish brown, and produces sulphate of potash, sulphurous acid, and iodine. (H. Rose, *Pogg.* 38, 121.)

$$KI + 2SO^3 = KO, SO^3 + SO^2 + I.$$

Distilled with dilute sulphuric acid, it yields first hydriodic acid—then, on further concentration, iodine, which dissolves in the hydriodic acid—and sulphurous acid, which passes over with the water and iodine, and is converted into sulphuric acid. Heated with peroxide of manganese and oil of vitriol, it yields iodine only, no sulphurous acid. A mixture of equal parts of iodide of potassium, common salt, nitre, and oil of vitriol, yields chloride of iodine as the principal product. (Soubeiran.) Steam passed over iodide of potassium heated to redness, causes the evolution of a large quantity of hydriodic acid gas; the residue is alkaline. (Schindler, *Mag. Pharm.* 31, 33.) A mixture of iodide of potassium and sal-ammoniac yields, when heated, sal-ammoniac, free iodine, and iodide of ammonium, whilst iodide and chloride of potassium remain behind. The mixture remains unaltered in dry air, but in moist air slowly absorbs water

and becomes brown through the decomposition of the hydriodate of ammonia which forms. (A. Vogel, *J. pr. Chem.* 22, 144.)

Iodide of potassium deliquesces only in very moist air; but more readily if mixed with carbonate of potash or other deliquescent salts. It dissolves in water with production of cold, which may amount to 24° (75·2° F.). One part dissolves at 12·5° in 0·735 parts, and at 16° in 0·709 parts of water (Baup); at 18° in 0·7 parts, and at 120° in about 0·45 parts of water. (Gay-Lussac.) A saturated solution boils at 120°. (Baup.) It dissolves, at 12·5°, in 5·5 parts of alcohol of specific gravity 0·85, and at 13·5° in between 39 and 40 parts of absolute alcohol; hot alcohol dissolves a much larger quantity, and deposits it in needles as it cools. (Baup.) The colourless aqueous solution, which may be considered as a solution of *hydriodate of potash*, yields crystals of iodide of potassium when evaporated. A dilute solution is coloured yellow by a small quantity of chlorine, but is rendered colourless by more; if, however, bromide of potassium is present, the yellow colour arising from the bromine remains. (Simon, *Repert.* 65, 200.) It colours paper bleached by chlorine, brown. (Baup.) The brownish yellow colour produced by chlorine is visible in a solution diluted to the extent of one part of iodide of potassium in 3000 parts of water; the same reaction is produced by sulphuric and nitric acid in a solution of one part in 6000 parts of water; the red precipitate with bichloride of platinum, with one part in 12000 parts of water; and the greenish yellow precipitate with nitrate of mercurous oxide, with one part in 60,000 parts of water. (Dublanc, *J. Chim. Med.* 2, 120.)

B. Biniodide of Potassium or Hydriodite of Potash.—A solution of 100 parts of iodine in 400 parts of water rapidly dissolves 76·5 parts or an additional atom of iodine: in a more dilute solution, the same quantity of iodine is more slowly dissolved (Baup). The liquid is dark reddish brown and neutral, and loses the excess of iodine by boiling or exposure to the air. (Gay-Lussac.) According to Girault (*J. Pharm.* 27, 390), it is necessary to evaporate to dryness and raise the temperature almost to the melting point to get rid of all the excess of iodine. A solution of 100 parts of iodide of potassium in 200 parts of water dissolves 153 parts (2 atoms) of iodine, forming a blackish brown metallic-looking liquid, which exhibits a very dark red colour by transmitted light, and throws down half of the dissolved iodine on the addition of water. (Baup.)

C. Iodite of Potash?—*a*. If equal atoms of iodine and ordinary hydrate of potash (containing carbonic acid) are dissolved in water—the dark-brown solution evaporated to dryness, without sufficient heat to drive off oxygen,—and the mass dissolved in water, evaporated, and left slowly to cool,—a number of very large crystals are obtained, differing from those of iodide of potassium and iodate of potash. Alcohol dissolves out iodide of potassium from them, leaving iodate of potash; and water forms with them a solution in which iodide of potassium and iodic acid can be detected. It is therefore a salt analogous to the soda-salt of Mitscherlich. (Reimann, *Mag. Pharm.* 23, 89.)

*b*. A cold aqueous solution of carbonate of potash forms with a little iodine a colourless liquid which smells of iodine; with more iodine it forms a brownish red solution; no carbonic acid is evolved, because bicarbonate of potash is produced. The brown solution when heated evolves vapour of iodine, with which, when the liquid boils, carbonic-acid gas is at first associated. By evaporating, redissolving, [illegible]ing off the

iodine three times in succession, all the carbonate of potash may be converted into iodide of potassium and iodate of potash. (Reimann.) [The solution first obtained in the cold may contain iodite of potash.]

*c.* By heating hydrate of potash with iodine to a temperature of 200° at most, iodide of potash is formed. (Grouvelle.)

D. Iodate of Potash.—The basic salt of Gay-Lussac, prepared by mixing the simple salt with potash, Rammelsberg failed in obtaining—the normal salt crystallizing out.

*a.* Mono-Iodate.—When iodine is added to a solution of potash, heat is evolved and 1 atom of iodate of potash together with 5 atoms of iodide of potassium or hydriodate of potash is formed.

$$6KO + 6I = KO,IO^5 + 5KO.$$

—1. To a solution of potash iodine is added till a permanent brown colour is just produced—the liquid evaporated to dryness—and the iodide of potassium separated from the residue by means of alcohol of specific gravity 0·81. Should the remaining iodate of potash contain carbonate, the latter is decomposed by acetic-acid, the whole evaporated, and the acetate of potash removed by alcohol. (Gay-Lussac.)—2. Terchloride of iodine is dissolved in solution of potash. (Berzelius.) In this process, iodide of potassium and chloride of potassium are formed at the same time; the latter on account of its smaller solubility in alcohol, is more difficult to separate.

$$3ICl^3 + 12KO = 2KO,IO^5 + 9KCl + KI.$$

—3. Iodide of potassium is fused in a hessian crucible, and allowed to cool till it becomes semi-fluid, and then $1\frac{1}{2}$ parts of chlorate of potash are added by degrees. The mass becomes fluid, swells up and solidifies to a spongy mixture of iodate of potash and chloride of potassium. It is dissolved in hot water, the iodate of potash left to crystallize, the crystals dissolved in water, and the iodate precipitated by alcohol. (O. Henry, *J. Pharm.* 18, 345; also *Schw.* 65, 442.)—Small, white, cubic crystals, apparently unaltered in the air. (Gay-Lussac.)

| | | Calculation. | |
|---|---|---|---|
| KO | 47·2 | | 22·14 |
| $IO^5$ | 166·0 | | 77·86 |
| KO,IO | 213·2 | | 100·00 |

Iodate of potash melts and froths up at a low red-heat and is converted, with escape of 22·59 per cent. of oxygen-gas, into quietly fusing iodide of potassium, yielding 77·41 per cent. of that salt. (Gay-Lussac.) If a part only of the oxygen is expelled, the residue contains simply iodide of potassium and iodate of potash, no periodate. (Rammelsberg.) According to Herzog (*N. Br. Arch.* 14, 90), the iodate of potash heated to redness in a glass tube, evolves, not only oxygen-gas, but likewise vapour of iodine, and leaves an alkaline residue. Iodate of potash detonates on burning charcoal with a purple light. (Gay-Lussac.) When dissolved in water, it is converted by sulphuretted hydrogen gas—with precipitation of sulphur and formation of a larger quantity of sulphuric acid,—first into brown hydriodite, then into colourless hydriodate of potash. (H. Rose.) Sulphurous acid likewise colours the solution brownish red at first, and afterwards decolorizes it again. (Reimann.) Arsenious acid reduces iodine from the solution. (Simon, *Repert*, 65, 209.)—Concentrated hydrochloric

acid added to this salt produces water, chlorine, and the compound of ter-chloride of iodine with chloride of potassium:

$$KO, IO^5 + 6HCl = KCl, ICl^3 + 6HO + 2Cl. \quad (Filhol.)$$

A solution of the salt in excess of boiling nitric acid yields crystals of iodic acid on cooling, while nitre remains in solution; if however it is evaporated to dryness, one-half the nitre formed is decomposed, and there remains a mixture of one atom of nitre and one atom of biniodate of potash. When greater heat is applied, all the nitric acid is decomposed into hyponitric acid and oxygen, and driven off, so that the residue consists merely of simple iodate of potash. (Penny, *Ann. Pharm.* 37, 203; also *J. pr. Chem.* 23, 297.) If iodide of potassium is mixed with a solution of this salt, stronger acids precipitate iodine from it; acetic acid produces only a brownish red colour, from formation of hydriodite of potash. (Reimann.) It dissolves in 13 parts of water at 14° (57·2° F.) (Gay-Lussac); more readily in a solution of iodide of potassium (Girault), and is not soluble in alcohol.

*b. Bin-iodate.*—The aqueous solution *a*, mixed with hydrochloric acid, gives on the addition of alcohol a precipitate of *b*.—2. An aqueous solution of ter-chloride of iodine is incompletely saturated with caustic potash, or carbonate of potash, on which the mixture becomes heated; and on cooling, a compound of *b* with chloride of potassium crystallizes out (the mother-liquor saturated with potash still yields the salt *a*). The solution of the above compound diluted with much water, and evaporated in the air at 25° (77° F.) yields the salt *b* in beautiful crystals. Transparent and colourless rhombic prisms, with dihedral summits, having a sour, astringent taste, and reddening litmus. When heated, it evolves oxygen gas and vapour of iodine, and passes first into simple iodate of potash, and then into iodide of potassium. Detonates on burning charcoal. Soluble in 75 parts of water at 15°; insoluble in alcohol. (Serullas, *Ann. Chim. Phys.* 22, 181; 43, 144; 45, 59.)

Calculation, according to Serullas.

| | | | |
|---|---|---|---|
| KO | 47·2 | ..... | 12·44 |
| $2IO^5$ | 332·0 | ..... | 87·56 |
| $KO, 2IO^5$ | 379·2 | ..... | 100·00 |

According to Penny, the crystals contain one atom of water.

*c. Ter-iodate.*—Formed on mixing an aqueous solution of iodic acid with a small quantity of potash, or by adding iodate or biniodate of potash dissolved in water to phosphoric, sulphuric, hydrochloric, nitric, or hydrofluosilicic acid. Iodate of potash in solution is heated with a large excess of dilute sulphuric acid, and left to evaporate in the air at 25°; the salt then crystallizes out. The mother-liquor contains a compound of bisulphate and biniodate of potash (*vid. seq.*). Large, transparent, colourless, rhombohedral crystals, which, even when free from sulphuric acid, assume a reddish colour after a time. When heated to fusion it evolves oxygen gas together with $\frac{2}{3}$ of its iodine, leaving iodide of potassium. It dissolves in 25 parts of water at 15°; the solution yields, on evaporation, crystals, first of the bi-acid, and then of the ter-acid salt. (Serullas, *Ann. Chim. Phys.* 43, 117.)

Calculation, according to Serullas.

| | | | |
|---|---|---|---|
| KO | 47·2 | ..... | 8·66 |
| $3IO^5$ | 498·0 | ..... | 91·34 |
| $KO, 3IO^5$ | 545·2 | | |

E. Periodate of Potash—*a. Sub-salt.*—A solution of *b* is mixed with potash and evaporated till crystallization commences. Small white crystals, which are anhydrous, and separated by heat into 22·188 per cent. of oxygen, and 77·735 per cent. of a mixture of potash and iodide of potassium; not less soluble in water than *b*.

*b. Normal Salt.*—Chlorine gas is passed through a solution of iodate of potash mixed with caustic potash or carbonate of potash. The salt separates in small, white crystals, decomposed by heat into 27·134 per cent. of oxygen and 72·95 per cent. of iodide of potassium, but slightly soluble in water, and having the properties of perchlorate of potash. (Magnus & Ammermüller, *Pogg.* 28, 521.)

| Calculated proportions of *a*. | | | | Calculated proportions of *b*. | | | |
|---|---|---|---|---|---|---|---|
| 2KO | 94·4 | | 34·16 | KO | 47·2 | | 20·59 |
| $IO^7$ | 182·0 | | 65·84 | $IO^7$ | 182·0 | | 79·41 |
| 2KO, $IO^7$ | 276·4 | | 100·00 | KO, $IO^7$ | 229·2 | | 100·00 |

## Potassium and Bromine.

A. Bromide of Potassium.—Potassium unites with bromine, producing violent inflammation and detonation, and breaking the glass tube employed in the experiment. Heated potassium decomposes hydrobromic acid gas; vapour of bromine expels iodine from iodide of potassium in a state of fusion. (Balard.)—*Preparation.*—1. Solution of hydrobromic acid is saturated with potash and evaporated. (Balard.)—2. A solution of bromide of iron is decomposed by carbonate of potash in equivalent proportions, boiled till the precipitate becomes brown, then filtered and evaporated. (O. Henry, *J. Pharm.* 15, 54.)—3. From the potash solution obtained in the preparation of bromine according to the first method (II., 273), the bromate of potash is separated from the bromide of potassium by crystallization, and the latter purified by ignition from the bromide of carbon which adheres to it.—4. Bromine is dissolved in solution of potash till the liquid becomes permanently coloured: the solution is then evaporated, the residue heated to redness and redissolved in water, the liquid saturated completely with hydrobromic acid, and evaporated again.—5. Through this solution of bromine in potash, sulphuretted hydrogen gas is passed in excess, in order to convert all the bromate of potash into hydrobromate—the excess of sulphuretted hydrogen is expelled by boiling—the solution filtered from sulphur—any excess of hydrobromic acid present being neutralized with potash, or of potash, on the contrary, with hydrobromic acid—and evaporated to a small bulk. (Löwig.) —The salt sometimes contains iodide of potassium. (*J. Chim. Med.* 18, 605.)

It crystallizes from an aqueous solution in very brilliant cubes, sometimes elongated into prisms or reduced to a tubular form. (Balard.) Seldom found in octahedrons. (Manx, *Schw.* 49, 103, and 249.) Decrepitates in the fire and fuses without decomposition; taste, sharp. (Balard.) sp. gr. = 2·415. (Karsten.)

| | Calculation. | | Balard. | Liebig. |
|---|---|---|---|---|
| K | 39·2 | 33·33 | 34·44 | 32·58 |
| Br | 78·4 | 66·66 | 65·56 | 67·42 |
| K, Br | 117·6 | 100·00 | 100·00 | 100·00 |

100 parts of bromide of potassium yield 160·3 parts of bromide of silver. (Liebig.) It is decomposed at a red heat by chlorine, but not by iodine. With solution of hypochlorous acid, it yields bromate of potash and chloride of potassium, chlorine and bromine being set free. (Balard.) When it is fused with chlorate of potash, bromate of potash is produced. (O. Henry.) It dissolves in water with production of cold, and more abundantly in hot than cold water, so that from a solution saturated while hot, bromide of potassium crystallizes on cooling. Slightly soluble in alcohol. (Balard.)

B. Perbromide of Potassium or Hydrobromite of Potash?—According to Balard, bromine is not more soluble in an aqueous solution of bromide of potassium than in pure water; according to Löwig, on the contrary, a solution of one part of bromide of potassium in 6 parts of water takes up as much bromine as it already contains, forming a reddish liquid, which, when gently heated, becomes colourless from the separation of the bromine dissolved. A solution of one part of bromide of potassium in one part of water takes up twice as much bromine as it already contains, evolving so much heat that the excess of bromine escapes with effervescence, and leaves a thickish dark-brown liquid which mixes with water without separation of bromine, but gives up its bromine when heated or exposed to the air.

C. Hypobromite of Potash? Concentrated solution of potash takes up bromine, with considerable rise of temperature, and forms a liquid which, when the potash is in excess, is of a pale-yellow colour, smells like chloride of lime, bleaches litmus and indigo, yields but a very small quantity of bromate of potash, and from which the weakest acids, even carbonic acid, liberate bromine: ammonia added to it gives off nitrogen gas. As soon as an excess of bromine is added, the liquid deposits a large quantity of potash, and after the free bromine present has escaped into the air, no longer possesses bleaching properties. Light, heat, and, to a certain extent, evaporation in vacuo, also destroy this power by causing the formation of bromate of potash. In the beginning there is doubtless formed a mixture of bromide of potassium and hypobromite of potash; afterwards, when excess of bromine is added, bromide of potassium and bromate of potash are produced. Carbonate of potash behaves in the same manner; with a deficient quantity of bromine it forms a bleaching liquid which likewise contains bicarbonate of potash; and with excess of bromine it yields bromide of potassium and bromate of potash. Bromine expels carbonic acid from bicarbonate of potash. (Balard, *J. pr. Chem.* 4, 165.) When bromine is carefully added, with constant stirring, to a cooled solution of potash, so that the latter may remain cold and in excess, no bromate of potash is obtained, but an orange-yellow bleaching liquid, which does not smell of bromine, evolves none when boiled, and behaves like the chlorides of the alkalis. (Fritzsche, *J. pr. Chem.* 24, 291.) Löwig also obtained with solution of carbonate of potash and bromine, a yellowish solution, which destroyed vegetable colours, corroded paper, smelt like chloride of potash, evolved carbonic acid when boiled, and deposited bromate of potash as it cooled, thereby losing its bleaching power.

D. Bromate of Potash. Formed by saturating a moderately concentrated solution of potash (or carbonate of potash, if heated) with bromine or chloride of bromine. The greater part of the brom crystal-

lizes out immediately, the rest by evaporation and cooling, whilst nearly all the bromide or chloride of potassium remains in solution. (Balard.)

Purified by repeated crystallization. This salt, on cooling from a hot solution, crystallizes in needles; by spontaneous evaporation, in flat plates (Balard); by very slow cooling from a warm solution, in four and six-sided tables and cubes with rounded summits. (Löwig.) Always in forms belonging to the regular system. (Fritzsche.)

| | Crystallized. | | Rammelsberg. |
|---|---|---|---|
| KO | 47·2 | 28·50 | 28·765 |
| $BrO^5$ | 118·4 | 71·50 | 71·235 |
| KO, $BrO^5$ | 165·6 | 100·00 | 100·000 |

At a red heat it separates into oxygen gas, and 90·04 per cent. of bromide of potassium. (Balard.) Before this decomposition takes place, the crystals generally decrepitate in a peculiar and violent manner—probably due to their conversion into a mixture of perbromate and bromite of potash. (Fritzsche, *J. pr. Chem.* 24, 285.)

$$2(KO, BrO^5) = KO, BrO^7 + KO, BrO^3.$$

This decrepitation is produced by those crystals only which are obtained from a solution, either perfectly neutral, or mixed with acetic acid and left to spontaneous evaporation. An excess of potash in the liquid causes the formation of crystals which do not possess this property. The crystals heated in a test tube to between 100° and 150°, lose a little water with slight decrepitation; but at about 350°, they crumble to powder with brisk detonation. The loss of weight (partly arising from the escape of water) of the salt dried at 107°, amounts, after decrepitation, to 1·35 per cent. only. The powder produced by decrepitation appears under the microscope to be composed of opaque pieces of ill defined shape, and presenting numerous fissures. It dissolves in water with evolution of small bubbles of oxygen gas, which appear even when it has been freed from adhering air by being moistened with alcohol, and continue to escape till the whole is dissolved. The quantity of oxygen evolved is very small, and is again partly absorbed by the solution, so that when the evolution of gas begins to slacken, some of the bubbles may, by examination with the microscope, be seen to disappear again. In hot water, the escape of gas is more abundant. In assuming that the bromate of potash in decrepitating is resolved into a mixture of perbromate and bromite of potash, it must further be supposed that the perbromate is decomposed by water into bromate of potash and oxygen gas, and that the bromite set free at the same time reabsorbs a portion of the oxygen gas, and is converted into bromate of potash; the excess of bromite absorbing from the air the oxygen which is required for this purpose. The crystals obtained by rapidly cooling a hot solution, or from the evaporation of a solution supersaturated with potash, decrepitate but slightly, and only at a higher temperature, near the melting point of the salt, and are reduced to a powder which evolves but little gas when dissolved in water. (Fritzsche.)

When the salt is gradually heated and begins to evolve oxygen gas, a faint glow makes its appearance at one point, and gradually extends over the whole mass, the evolution of gas at the same time becoming more rapid; bromide of potassium in a half fused state remains behind. (Rammelsberg.)—The salt detonates on ignited charcoal, and violently when mixed with sulphur and struck (Balard); also by the electric spark.

(Löwig.) It is decomposed by oil of vitriol, with violent decrepitation (which might seem to indicate the presence of a gas in the nascent state, similar to oxide of chlorine) into vapour of bromine, oxygen gas, and sulphate of potash. Mixed with sulphur, resin, &c. it inflames when touched with oil of vitriol. (Löwig.) When heated with nitric acid it is resolved into vapour of bromine, oxygen, and nitrate of potash. (Penny, *J. pr. Chem.* 23, 298.) From a hot aqueous solution of the salt mixed with sulphuric acid, bromate of potash (no bibromate) crystallizes out first, and afterwards bisulphate of potash. (Rammelsberg.) The cold aqueous solution treated with hydrosulphuric acid, yields milk of sulphur, sulphuric acid, and hydrobromic acid. (H. Rose.) Chlorine passed through the solution produces but slight decomposition, merely separating a little bromine, which colours the liquid yellow. (Rammelsberg.) The salt dissolves at 15° in 15·2 parts of water, (Rammelsberg,) more abundantly in hot water, very sparingly in alcohol. (Balard; also Rammelsberg. *Pogg.* 52, 80; 55, 88.)

## Potassium and Chlorine.

A. Chloride of Potassium.—*Digestive Salt, Double refined culinary Salt, Sal digestivum Sylvii, Sal febrifugum Sylvii.*—Potassium takes fire at ordinary temperatures in chlorine gas, and burns with a red flame, and more vividly than in oxygen gas; the product is chloride of potassium. (H. Davy.) Chlorine gas passed over red-hot potash or iodide of potassium, forms chloride of potassium, and liberates oxygen or iodine. Potassium gently heated in hydrochloric acid gas burns with a lively red flame, producing chloride of potassium, and separating half a volume of hydrogen gas. When concentrated hydrochloric acid is dropped upon hydrate of potash in the dark, a faint light is emitted. (Henrich.) Potassium separates the chlorine from chloride of magnesium, and likewise from many other chlorides of the earth-metals and the heavy metals.—Chloride of potassium is occasionally obtained as a by-product, in the preparation of chlorate of potash, soap, glass, solution of carbonate of ammonia, carbonate of soda, and tartaric acid, and in the purification of nitre.

White, crystallizing in cubes often prismatically elongated, and rarely—*e. g.* from potash-ley—in octohedrons. Specific gravity = 7·836 (Kirwan), = 1·9153 (Karsten), = 1·945 (Kopp). Unacted on by the air. Decrepitates when heated; fuses at a low red heat; volatilizes at a higher temperature unchanged. It is somewhat more volatile than chloride of sodium; in a covered crucible, it may be kept in a state of fusion without loss; in open vessels, it volatilizes gradually in the constantly renewed current of air. (H. Rose; *Pogg.* 31, 132. *Vid.* I., 266.) Tastes like common salt.

| | Calculation. | | Ure. |
|---|---|---|---|
| K | 39·2 | 52·6 | 53 |
| Cl | 35·4 | 47·4 | 47 |
| K, Cl | 74·6 | 100·0 | 100 |

| | Berzelius. | Kirwan. | H. Davy. | Wenzel. | Curaudau. | Dalton. | V. Rose. | Berthollet. |
|---|---|---|---|---|---|---|---|---|
| KO | 63·257 | 64 | 64·4 | 64·74 | 65·17 | 65·6 | 66·03 | 66·66 |
| $MnO^2$ | 36·743 | 36 | 35·6 | 35·26 | 34·83 | 34·4 | 33·97 | 33·34 |
| KO, $MnO^2$ | 100·000 | 100 | 100·0 | 100·00 | 100·00 | 100·0 | 100·00 | 100·00 |

[$MnO^2$ signifies hypothetically anhydrous muriatic [illegible] an atomic weight = 27·4. *Vid.* II. 356.]

Sulphur mixed with chloride of potassium in a fused state produces a small quantity of sulphide of potassium. (A. Vogel, *Schw.* 21, 71.) Hydrated sulphuric, tartaric, and nitric acids, form a salt of potash, and separate hydrochloric acid.—Chloride of potassium, in dissolving in water, produces a much greater degree of cold than common salt, but less than sal-ammoniac. One part of the salt dissolves at 17·5° (63·5° F.) in 3·008 parts of water, forming a solution of specific gravity 1·1635 (Karsten): it dissolves at 11·8°, in 2·89 parts; at 13·8°, in 2·87 parts; and at 15·6°, in 2·85 parts of water. (Kopp.) 100 parts of water at 0° dissolve 29·23 parts of chloride of potassium, and for every degree above zero (centigrade) 0·2738 parts. (Gay-Lussac.) From the solution—in which hydrochlorate of potash may be supposed present—chloride of potassium again crystallizes on evaporation. It is but slightly soluble in alcohol.

B. Hypochlorite of Potash.—a. *Pure.*—A solution of hypochlorous acid in water unites with solution of potash, producing a rise of temperature. To a solution of potash kept quite cool, the aqueous acid is added by degrees, in such quantity that the potash may remain slightly in excess.—Heat or an excess of acid would cause the compound to separate into chloride of potassium and chlorate of potash. (Balard.)—Hitherto known only in the state of solution, having the properties already described. (II., 301—304.)

b. *Chloride of Potash.* An aqueous solution of one atom of hypochlorite of potash and one atom of chloride of potassium; *Eau de Javelle.* 1. Chlorine is passed through an aqueous solution of caustic potash or its carbonate, kept constantly cool, till the potash is all but saturated. The carbonate of potash at first changes, from loss of alkali, into the bicarbonate, which crystallizes from the solution when more saturated; but by a greater quantity of chlorine, this salt is likewise changed into chloride of potash, with escape of carbonic acid. If the liquid becomes heated, or if more than one atom of chlorine is supplied to each atom of potash, the hypochlorite of potash is decomposed, and the bleaching property —at least in part—is lost.—2. Solution of chloride of lime is mixed with carbonate of potash, and the clear liquid decanted.—Colourless liquid, having a peculiar smell and rapidly destroying organic colours and odours—corroding paper, with disengagement of heat—evolving oxygen when boiled—decomposing ammonia with escape of nitrogen gas—oxidizing metals, &c.—(See II., 300—304.) If chlorine—produced from a mixture of 10 parts of common salt, 8 parts of manganese, 14 parts of oil of vitriol, and 10 parts of water—is passed through 24 parts of dry powdered carbonate of potash moistened with one part of water, the bleaching compound is obtained in the solid form, mixed with bicarbonate of potash. (Ph. Mayer & Schindler, *Repert.* 31, 1.)

¶ C. Chlorite of Potash. Prepared by saturating caustic potash with chlorous acid. The acid takes some time to combine with the alkali, the combination not being complete for several hours. On agitating the mixture, the colour of the acid disappears; but on adding a few drops of solution of acetate of lead, a white precipitate is formed, containing excess of oxide of lead, and quickly changing (in the liquid) into chloride and brown peroxide of lead. But if the lead-salt be added after the acid and alkali have been mixed for an hour, yellow scales of chlorite of lead are precipitated and remain unaltered.—If the acid is added in excess, the liquid acquires a deep-red colour, and a bichlorite of

potash is formed: this salt cannot, however, be obtained in the solid state, because the excess of acid escapes on evaporation. To make sure that the potash is completely saturated, the chlorous acid must be added till the liquid begins to exhibit a red tint; it must then be evaporated to dryness over the water-bath as quickly as possible. The residue then consists of neutral chlorite of potash, $KO, ClO^3$. But if the liquid is evaporated slowly, either in vacuo or in the drying chamber, the salt is transformed into a mixture of chloride of potassium and chlorate of potash.

$$3(KO, ClO^3) = KCl + 2(KO, ClO^5).$$

The dry salt is colourless, and may be preserved unchanged in close vessels. When exposed to the air, it deliquesces, and undergoes gradual decomposition. In a dry atmosphere, it supports a temperature of 160° without alteration; but at higher temperatures, it undergoes a change not yet understood, and acquires a yellow colour. (Millon, *Ann. Pharm.* 46, 306; Berzelius, *Traité*, 3, 135.) ¶

D. Hypochlorate of Potash.—Solution of potash not quite saturated with peroxide of chlorine is evaporated in vacuo.—Crystallizes in fine scales, similar to those of chlorate of potash; but when mixed with one part of oil of vitriol and 10 parts of water, it evolves peroxide of chlorine, with violent effervescence. It absorbs carbonic acid gas, and is decomposed by it. Deliquesces only in moist air. (Martens, *vid.* II. 311, 312.) According to Millon, peroxide of chlorine yields with potash a mixture of chlorate of potash ($KO, ClO^5$), and chlorite of potash ($KO, ClO^3$).

E. Chlorate of Potash.—*Hyper-oxymuriate of potash.*—A solution of one part of potash in 3 parts of water is completely saturated with chlorine passed into it through a bent tube; it is then allowed to stand a whole day—or heated for some time, not quite to the boiling point—in order to decompose all the hypochlorite of potash. On cooling, the greater part of the chlorate of potash crystallizes out—most completely, however, at freezing temperatures. (*Sch.* 33 and 34.)

$$6KO + 6Cl = 5KCl + KO, ClO^5.$$

or: $$6KO + 6Cl + 5HO = 5(KO, HCl) + KO, ClO^5.$$

On heating the liquid, it evolves a small quantity of oxygen—at most, however, from 2 to 3 per cent. (Gay-Lussac.) Protracted boiling is necessary, by which chlorate of potash is lost. (Graham.) If one part of hydrate of potash is dissolved in 2, 4, or 16 parts of water—then, on saturating with chlorine and evaporating, oxygen escapes, and one atom of chlorate of potash is obtained with about 18 atoms of chloride of potassium. (Morin, *Ann. Chim. Phys.* 37, 154.) The liquid often becomes reddish from the manganese carried over by the chlorine, which forms hypermanganate of potash. The mother liquor when evaporated and cooled, still yields crystals of chlorate of potash, but contaminated, to a greater extent on each repetition of the process, with chloride of potassium: this must be got rid of by repeated solution in hot water and cooling, the chlorate being far more soluble in hot than in cold water, while the solubility of the chloride varies but slightly with the temperature. Mackenzie's assertion, that more chlorate is obtained when the chlorine gas passed into the solution is mixed with oxygen gas or air, so

that oxygen may be absorbed at the same time, appears to be unfounded. (II. 301.)

2. A solution of one part of carbonate of potash in 2 or 3 parts of water is saturated with chlorine gas, and then treated as in the first method. The first half of the chlorine is absorbed readily, bicarbonate of potash being formed at the same time; this salt, however, solidifies, and may stop up the conducting-tube. After this the absorption proceeds more slowly, and chlorine and hypochlorous acid escape together with the carbonic acid which is given off during the remainder of the process. Caustic potash is therefore preferable. Guthrie (*Sill. Am. J.* 21, 94) used 10 parts of oil of vitriol (with salt and manganese) in the first process, and 17 parts in the second, to obtain one part of chlorate of potash. The silica frequently contained in carbonate of potash is thrown down by the chlorine, and mixes with the crystals of chlorate of potash. In this process, also, the liquid is often coloured reddish by hypermanganate of potash.

3. Chlorine gas is passed to saturation through an intimate mixture of one atom (69·2 parts) of carbonate of potash and one atom of dry hydrate of lime (containing 28 parts of burnt lime). Absorption proceeds rapidly, the temperature rising above 100°, and the water passing off in vapour. The saturated mass is heated,—so as to decompose any hypochlorite of potash that may be present—dissolved in water, filtered, and left to crystallize. (Graham, *Phil. Mag. An.* 18, 318; also *Ann. Pharm.* 41, 306.) All the lime remains in the form of carbonate. The neutral filtrate, which has no bleaching power, contains only chloride of potassium and chlorate of potash. (Graham.)

4. A mixture of one atom (74·6 parts) of chloride of potassium and 6 atoms (168 parts) of burnt lime, reduced with water to a thin cream, is saturated with chlorine, and the chlorate of potash separated by crystallization from the chloride of calcium, the only other substance present. (Liebig, *Ann. Pharm.* 41, 307.)

$$KCl + 6CaO + 6Cl = KO, ClO^5 + 6CaCl.$$

5. 10 parts of chloride of lime, made into a paste with water, are evaporated to dryness, by which means the chloride is converted into a mixture of chlorate of lime and chloride of calcium, no longer possessing bleaching properties. It is then dissolved in water and filtered; the solution concentrated by evaporation; mixed with one part of chloride of potassium; and allowed to cool. The chlorate of potash, amounting to about 0·83 parts, which crystallizes out, is purified from chloride of calcium by repeated crystallization. (Liebig, *Mag. Pharm.* 35, 225.) A saving of $\frac{4}{5}$ of potash is effected in this process; but the rapid evolution of oxygen during the evaporation of the chloride of lime occasions the loss of a large portion of the chlorate ($\frac{2}{3}$, according to Martens).—Vée (*J. Pharm.* 19, 270) mixes solution of chloride of lime, without previously heating it, with chloride of potassium; boils rapidly, by which, however, much oxygen is often driven off; and leaves it to crystallize. [Saturating the liquid with chlorine previously to boiling it, might be serviceable.]

6. Solution of chloride of lime is precipitated by carbonate (or sulphate) of potash, the solution saturated with chlorine, evaporated, and cooled. (Gay-Lussac, *Compt. rend.* 14, 951.) The crystals are separated by solution in hot water and filtration, from silica and oxide of manganese, and by crystallization—repeated till the salt no longer

renders a solution of silver turbid—from the chlorides of potassium and calcium.

Chlorate of potash forms colourless transparent crystals, having a glassy lustre, and belonging to the oblique prismatic system of crystallization. Softer than rock salt; cleavable parallel to $u$ and $u^1$;—$i : u$ or $u^1 = 105° 30'$; $u : u^1 = 104°$; $i : f = 106° 45'$, $i : \alpha = 129° 45'$. (Brooke, *Ann. Phil.* 21, 451.) Cleavable parallel to $u$, $u^1$ and $i$; $i : u$ or $u^1 = 106°$; $u : u^1 = 104°$ nearly; macle-crystals, with their angles in the same direction, produced by the union of two crystals at their $i$-surfaces; the crystals refract light doubly. (Haidinger, *Edinb. J. of Sc.*. 1, 103.) By rapid crystallization, the prisms are rendered very short and tabular; by slower crystallization, they are elongated. The salt emits sparks when rubbed in the dark; fuses at a gentle heat, without decomposition; remains unaltered in the air; tastes cooling, rough, and like nitre.

| | Crystallized. | | Berzelius. | Chenevix. |
|---|---|---|---|---|
| KO ..... | 47·2 ..... | 38·5 ..... | 38·4917 ..... | 39·2 |
| $ClO^5$ ..... | 75·4 ..... | 61·5 ..... | 61·5083 ..... | 58·3 |
| Water ..... | | | | 2·5 |
| KO, $ClO^5$ ..... | 122·6 ..... | 100·0 ..... | 100·0000 ..... | 100·0 |

Above 356°, but still under redness, it evolves oxygen gas with considerable frothing, and at a higher temperature is completely resolved into oxygen and chloride of potassium, the oxygen amounting, according to Stadion, to 38·5; Berzelius, 39·15; Pelouze, 39·16; and Marignac (*Ann. Pharm.* 44, 13), 39·161 per cent. A trace of chlorine is mixed with the oxygen, and of potash with the chloride. (Marignac.) But if the heat at which the oxygen begins to escape is not further increased, the mass ceases after a time to boil, becomes pasty, and consists of a mixture of perchlorate of potash and chloride of potassium in equal numbers of atoms. (Serullas, *Ann. Chim. Phys.* 46, 323; also *Pogg.* 22, 301.)

$$2(KO, ClO^5) \quad KO, ClO^7 + KCl + 4O;$$

Probably, 2 atoms of chlorate of potash are resolved by the first action of the heat into 1 atom of perchlorate of potash and 1 atom of chlorite $= KO, ClO^3$; and this, by the evolution of 4 atoms of O, is converted into KCl. From 100 parts of chlorate of potash, 45 parts of perchlorate may be thus obtained. (Serullas.) For the complete decomposition of the perchlorate remaining in the residue, into oxygen gas and chloride of potassium, either a stronger heat is necessary, or the addition of powdered manganese: this substance causes, even at a moderate heat and without itself losing oxygen, a rapid escape of gas from the salt, followed indeed by an increase of heat, which raises the mass to low redness. (Döbereiner, *Ann. Pharm.* 1, 236; *vid.* II., 20.) Oxide of copper acts like manganese; silica produces no effect. (Mitscherlich, *Pogg.* 55, 220.)

Chlorate of potash detonates with combustible bodies, as carbon, phosphorus, oxide of phosphorus, sulphur, various metals and metallic sulphides; the explosion being extremely violent, often induced even by a blow, and, when large quantities are used, attended with great danger. A mixture of the salt with arsenic or sulphide of antimony is not inflamed by a red-hot iron-wire in vacuo; the first mixture inflames, however, on the admission of nitrogen gas, when the barometer stands at 2 inches only; and the second, on a larger admission of nitrogen gas; but all combustible mixtures of this kind inflame under smaller pressure in nitrogen than in air. (Hearder, *J. pr. Chem.* 20, 253.) Chlorate of potash when fused

with oxide of lead changes it into peroxide; and a mixture of hydrate of potash and peroxide of manganese converts it into manganate of potash.

It is decomposed by oil of vitriol into oxide of chlorine, bisulphate of potash, and perchlorate of potash, the decomposition being attended with violent decrepitation, and often with a flashing light; combustible substances, such as sulphur, metallic sulphides, arsenic, resin, camphor, gum, or sugar, mixed with the salt and moistened with oil of vitriol, are inflamed by the oxide of chlorine evolved. A mixture of the salt with sulphur, sulphide of antimony, or arsenic, does not take fire in vacuo on the addition of oil of vitriol, but merely effervesces with emission of sparks, visible in the dark. (Hearder.) Chlorate of potash distilled with iodine, yields chloride of iodine which volatilizes, and chloride of potassium and chlorate and iodate of potash which remain behind. (Wöhler.) A boiling solution of the salt takes up the first atom of iodine added, without becoming coloured; but on a further addition of iodine, a yellow, and then a brown colour is produced: the products of the reaction are iodate of potash and a chloride of iodine, containing variable proportions of iodine.

$$KO,ClO^5 + I + xI = KO,IO^x + I^xCl.$$

With a small quantity of iodine, pentachloride of iodine appears to be formed; for on boiling, the liquid evolves chlorine, and afterwards contains terchloride of iodine, which yields a precipitate of iodine with carbonate of potash. On evaporating the liquid, the chloride of iodine escapes, whilst pure iodate of potash remains. (Millon, *J. Pharm.* 27, 102; also *J. pr. Chem.* 23, 253.) An aqueous solution of chlorate of potash mixed with iodic acid, yields, according to the quantity of iodic acid added, crystals of iodate or biniodate of potash—the mother-liquor contains chlorate of potash and free chloric acid. (Serullas, *Ann. Chim. Phys.* 45, 281.) An excess of concentrated nitric acid boiled with the salt, produces nitrate and perchlorate of potash, while chlorine and oxygen gas are evolved, but no chloric oxide.

$$4KO,ClO^5 + 3NO^5 = 3(KO,NO^5) + KO,ClO^7 + 3Cl + 13O.$$

(Penny, *Ann.* 37, 203; also *J. pr. Chem.* 23, 296.—Millon.) For the decomposition of 3 parts of chlorate of potash, 100 parts of nitric acid of specific gravity 1·327 are required. The decomposition is greatly accelerated by the presence of spongy platinum (which, however, is not itself acted upon), probably because it promotes a more rapid evaporation of the water, and thereby concentrates the acid. Dilute nitric acid does not act on chlorate of potash even when boiled, neither does the concentrated acid—when free from hyponitric acid—in the cold; but if a small quantity of hyponitric acid is present, the nitric acid on being mixed with the salt acquires a yellow colour by taking up peroxide of chlorine, and may cause explosion if distilled. Fuming nitric acid charged with hyponitric acid likewise produces—though very slowly at ordinary temperatures—chloric oxide, nitre, and perchlorate of potash. A solution of chlorate of potash in nitric acid rapidly oxidizes many substances, as sulphur, and selenium without frothing. (Millon, *J. Pharm.* 29, 184; *vid.* II., 305, 306.) Hydrosulphuric acid does not decompose an aqueous solution of chlorate of potash.

Chlorate of potash dissolves in water, producing a somewhat considerable degree of cold. One part dissolves at 0° in 30°, at 15° in 16·7, at 35° in 8·33, at 49° in 5·26, at 104° in 1·67 parts of water (Gay-

Lussac); and at 16° in 120 parts of alcohol, containing 83 per cent. (Wittstein.)

Mixture for *Lucifer Matches*, to be inflamed by oil of vitriol: 60 parts of chlorate of potash, 14 parts of sulphur, 14 parts of gum-benzoin, a small quantity of gum-tragacanth, and cinnabar; or: 30 parts of chlorate of potash, 10 parts of sulphur, 8 parts of sugar, 5 parts of gum-arabic, and a little cinnabar; the sulphur must be wetted, or great danger will be incurred in the mixing (a fatal explosion of this mixture is mentioned in *Repert.* 3, 119). Mixture for *Percussion-powder* (*Zündpulver*) for guns: 54 parts of chlorate of potash, 21 parts of nitre, 18 parts of sulphur, 7 parts of lycopodium; or 100 parts of chlorate of potash, 55 parts of nitre, 33 parts of sulphur, 17 parts of sifted touch-wood, and 17 parts lycopodium; or 20 parts of chase-powder (*Jagdpulver*) freed from nitre by means of water, and then mixed with 11 parts of chlorate of potash and water to the consistence of a thin paste. Gunpowder prepared with chlorate of potash, charcoal, and sulphur, acts too violently and inflames too easily. (*Vid.* Aubert, Pelissier & Gay-Lussac, *Ann. Chim. Phys.* 4, 216.)

F. Perchlorate of Potash.—Produced from the chlorate by electrolysis; by partial decomposition by heat, and by complete decomposition with sulphuric or nitric acid.—1. A solution of chlorate of potash is introduced into the voltaic circuit; perchlorate crystallizes out at the positive pole. (Stadion.)—2. Chlorate of potash is gently heated in a porcelain crucible till the melted mass ceases to evolve oxygen at the same temperature, and becomes thickish, and a portion taken out on a platinum-wire and powdered, communicates but a very slight yellow colour to concentrated hydrochloric acid,—a proof that nearly all the chlorate is decomposed. The cooled mass dissolved in hot water, deposits after a while the greater part of the perchlorate of potash, which must be purified by re-crystallization; the chloride of potassium and undecomposed chlorate remain in solution. If the heat be continued till the powdered test no longer colours concentrated hydrochloric acid at all, and is consequently quite free from chlorate, the perchlorate of potash may likewise be decomposed. (Serullas, *Ann. Chim. Phys.* 46, 325; also *Pogg.* 22, 301.) ¶ Millon (*Ann. Pharm.* 46, 315) asserts that by this method between 50 and 53 per cent. of perchlorate may be obtained, the theoretical quantity produced being 56 per cent., on the supposition that 2 atoms of chlorate of potash are resolved into 1 atom of perchlorate and 1 atom of chlorite. $(2KO, ClO^5) = KO, ClO^7 + KO, ClO^3$. ¶.—3. To 2 parts of oil of vitriol contained in a dish, 1 part of pounded chlorate of potash is added by degrees, and the yellow paste gently heated for 24 hours in a water-bath, till it has lost both its colour and the smell of chloric oxide; when cool, it is diluted with cold water; the perchlorate, amounting to $\frac{9}{32}$ parts (or 28 per cent.) of the chlorate of potash employed, is then collected on a filter, and purified from bisulphate of potash by repeated crystallization. (Stadion.) Mitscherlich (*Pogg.* 25, 298) gradually adds 1 part of chlorate of potash to 1 part of warm oil of vitriol. Penny recommends that the chlorate be heated with concentrated nitric acid; (III. 60), by which, however, 4 atoms of chlorate can be made to yield only 1 atom of perchlorate of potash.

Transparent, colourless, right rhombic prisms *Fig.* 53 and 54, the last also with the P-surface; $u : u^1 = 103° 55\frac{1}{2}'$; $i : i^1$ (in *Fig.* 54) $= 101° 19\frac{1}{3}'$. The prisms are sometimes elongated in the direction of the *u*-surface, sometimes in that of the *i*-surface. They contain only a small

quantity of mechanically combined water. (Mitscherlich.) The salt is perfectly neutral, and has a slight taste like that of chloride of potassium. (Stadion, *Gilb.* 52, 213.)

| | Calculation. | | Stadion. |
|---|---|---|---|
| KO | 47·2 | 34·05 | 34·31 |
| $ClO^7$ | 91·4 | 65·95 | 65·69 |
| $KO, ClO^7$ | 138·6 | 100·00 | 100·00. |

Perchlorate of potash is decomposed at a heat somewhat above 400°, yielding oxygen gas and chloride of potassium. The oxygen amounts, according to Mitscherlich, to 45·83; Stadion, 45·92; Marignac, 46·187; and Serullas, 46·21 per cent. Detonates slightly on glowing charcoal. Heated with oil of vitriol to 137°, it evolves perchloric acid. Dissolves in 65 parts of water at 15°, and in a smaller quantity of hot water; quite insoluble in alcohol. (Serullas, *Ann. Chim. Phys.* 46, 297, also *Pogg.* 22, 292.) Perchloric acid precipitates perchlorate of potash not only from solutions of the soluble potash-salts, but from those also of potash-alum and cream of tartar. (Serullas.) (Hence the perchlorate must require for solution more than 65 parts of cold water.)

F. Sulphate of Chloride of Potassium.—Powdered chloride of potassium placed in a vessel surrounded with ice absorbs the vapours of anhydrous sulphuric acid, without any evolution of gas, forming a hard translucent mass, which evolves hydrochloric acid gas with violence on the addition of water; when heated alone, it fuses, evolves chlorine and sulphurous acid gas in equal measures, and is converted into sulphate of potash almost free from chlorine. (H. Rose, *Pogg.* 28, 120.)

G. Chloride of Iodine and Potassium. *Chloroiodite de potassium.* This compound is formed,—1. By mixing an aqueous solution of terchloride of iodine with chloride of potassium—or else with hydrochloric acid and then with potash or carbonate of potash—in such quantity that the liquid may still remain acid.—2. By adding iodine to an aqueous solution of chloride of potassium, and passing chlorine gas through it.—3. By saturating a strong solution of iodide of potassium with chlorine gas.

$$KI + 4Cl = KCl, ICl^3$$

—4. By the decomposition of iodate of potash by concentrated hydrochloric acid:

$$KO, IO^5 + 6HCl = KCl, ICl^3 + 2Cl + 6HO.$$

—5. By dissolving iodide of potassium and chlorate of potash in hot hydrochloric acid:

$$3KI + 2(KO, ClO^5) + 12HCl = 3(KCl, ICl^3) + 2KCl + 12HO.$$

With too large an excess of hydrochloric acid, the compound does not crystallize out on cooling.—6. By dissolving iodine and chlorate of potash in slightly warmed hydrochloric acid:

$$KO, ClO^5 + I + 6HCl = KCl, ICl^3 + 3Cl + 6HO.$$

—7. By passing chlorine through solution of potash in which so much iodine is diffused, that no free chloride of potassium is formed. (In this process, chlorate of potash is probably formed at the same time, or else the compound of chloride of potassium with biniodate of potash.) All these mixtures yield crystals of the compound on cooling.—1. A warm solution of chloride of potassium is mixed with terchloride of iodine dis-

solved in water.—2. One part of iodate of potash is dissolved in a flask (so that no chloride of iodine may be lost by evaporation), in 8 parts of hydrochloric acid of 22° Bm., at a temperature between 40° and 50°, and when the solution is complete, the liquid is left slowly to cool.—3. Through a warm solution of one part of iodide of potassium in 2 parts of water, to which a few drops of hydrochloric acid have been added, chlorine gas is passed to saturation. On cooling, the liquid solidifies in consequence of the formation of crystals. If the solution were used cold, the tube which conducts the chlorine would be choked up by the crystals: if the iodide contains free potash or carbonate of potash, a compound of chloride of potassium with the biniodate of potash of Serullas (*vid. seq.*) may also be precipitated. The mother-liquid is quickly poured off and the crystals produced immediately dried between folds of blotting-paper and put into well stopped bottles. By remaining in the mother-liquor, they would be changed into crystals of iodate of potash.

Long, golden-yellow, brilliant prisms, apparently of the oblique rhombic form. This compound smells intolerably of chloride of iodine, has a caustic taste, and corrodes the skin almost as powerfully as free chloride of iodine.

Calculation, according to Filhol.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $KCl^3$ | 74·6 | 24·31 | | K | 39·2 | | 12·78 |
| ICl | 232·2 | 75·69 | or: | I | 126·0 | | 41·07 |
| | | | | 4Cl | 141·6 | | 46·15 |
| $KCl, ICl^3$ | 306·8 | 100·00 | | | 306·8 | | 100·00 |

The crystals are anhydrous. When heated, the compound leaves 24·22 per cent. of chloride of potassium; the first portions of the terchloride of iodine escape undecomposed; the last are resolved into chlorine, protochloride of iodine, and free iodine. If the salt is not dry, but still retains some of the mother-liquor charged with hydrochloric acid, the chloride of iodine is more strongly retained, and is evolved only in the form of chlorine, protochloride of iodine, and free iodine. The compound is very soluble in water, and in solution, is rapidly converted into chloride of potassium and iodate of potash. (Other products must however be formed at the same time.) This salt when exposed to the air quickly diminishes in weight, loses its fine yellow tint, and becomes opaque in 24 hours. Alkalis precipitate iodine from its aqueous solution; chloride of barium produces a cloud in a few seconds, and precipitates iodate of baryta; nitrate of silver, when concentrated and supersaturated with nitric acid, throws down chloride and iodide of silver from the solution; when dilute it also precipitates iodate of silver. Ether separates the chloride of iodine from the crystals, and thereby deprives them of their smell and colour. (Filhol, *J. Pharm.* 25, 433 and 506.)

## Potassium and Fluorine.

A. Fluoride of Potassium. When hydrofluoric acid comes in contact with potassium, fluoride of potassium is formed, and hydrogen gas evolved, the action being attended with great rise of temperature. Potassium decomposes fluoride of boron, fluoride of silicium, and other metallic fluorides. A solution of hydrofluoric acid is mixed in a silver or platinum vessel, with caustic potash or carbonate of potash (Gay-Lussac & Thénard, *Recherch.* 2, 18), in such quantity that the acid slightly predominates,—the liquid evaporated, and the residue heated strongly to expel the excess

of acid. (Berzelius.)—Fluoride of potassium crystallizes from an aqueous solution, if evaporated under + 40°, in colourless cubes often lengthened into a prismatic form, or else exhibiting square, pyramidally excavated faces. Fuses below a red heat; has a sharp saline taste and alkaline reaction. When treated with oil of vitriol, even at ordinary temperatures, it evolves hydrofluoric acid with violent effervescence. Decomposed by chlorine.—Deliquesces rapidly in the air. (Berzelius, *Pogg.* 1, 10.)

Fluoride of potassium dissolves in water, causing a rise of temperature. The solution dims glass. It contains either fluoride of potassium, or hydrofluate of potash, or double fluoride of hydrogen and potassium, (bihydrofluate of potash) together with free potash, as its alkaline reaction indicates. (*Vid.* H. Rose, *Pogg. 55, 537.*) If the aqueous solution is evaporated by a gentle heat in a platinum dish till crystals form at the bottom, and then poured off from these, it solidifies, on cooling, to a mass of long, thread-like, radiating crystals. It is precipitated in a similar manner from a concentrated aqueous solution by strong alcohol. These crystals contain 39·44 per cent. of water. (H. Rose, *Pogg. 55, 554.*) They are either fluoride of potassium with 4 atoms of water, or hydrated hydrofluate of potash with 3 atoms of water.

Fluoride of potassium fused with silica forms a mass which is vitreous while fused and becomes milk-white as it cools; it is insoluble in alcohol. (Berzelius.)

| | Calculation. | | | | Hydrated crystals. | | | |
|---|---|---|---|---|---|---|---|---|
| K | 39·2 | ..... | 67·70 | | KF | 57·9 | ..... | 61·66 |
| F | 18·7 | ..... | 32·30 | | 4HO | 36·0 | ..... | 38·34 |
| KF | 57·9 | ..... | 100·00 | | KF, 4HO | 93·9 | ..... | 100·00 |

B. Fluoride of Hydrogen and Potassium.—Hydrofluoric acid is mixed with fluoride of potassium or with a quantity of potash not sufficient to neutralize it, and the liquid evaporated in a platinum dish. By spontaneous evaporation, it crystallizes in rectangular four-sided tables with truncated lateral edges; in a deeper vessel and by still slower evaporation, in cubes; if rapidly evaporated, it forms a solid transparent mass, consisting of broad crystalline plates which cross each other. Fuses when heated, and at the temperature of incipient redness, is converted, with evolution of hydrofluoric acid, into fluoride of potassium amounting to 74·9 per cent. Heated with 6 times its weight of protoxide of lead, it yields 11·6 per cent. of water. Dissolves easily in pure water, forming a solution of fluoride of hydrogen and potassium or of bihydrofluate of potash; difficultly soluble in water containing free hydrofluoric acid. (Berzelius.)

| | Calculation. | | | Berzelius. |
|---|---|---|---|---|
| KF | 57·9 | ..... | 74·61 | ..... 74·9 |
| HF | 19·7 | ..... | 25·39 | ..... 25·1 |
| KF, HF | 77·6 | ..... | 100·00 | ..... 100·0 |

C. Fluoboride of Potassium.—1. On mixing tetrahydrofluate of boracic acid with any salt of potash dissolved in water, a gelatinous precipitate falls, which resembles a newly formed precipitate of fluoride of silicium and potassium, even in the play of colours which it exhibits when a certain excess of acid is present.—2. 100·2 parts (one atom) of bicarbonate of potash dissolved together with 61·8 parts (one atom) of crystallized boracid acid in excess of aqueous solution of hydrofluoric acid, and evaporated, yields, even to the last trace, nothing but fluoboride of

potassium. This therefore is the proper proportion; if more boracic acid is used, it remains in the mother-liquor. The mass obtained by the first process—when collected on a filter, washed with cold water, and pressed while still moist—feels gritty like hair-powder. When dry, it yields a fine white powder; it crystallizes from a hot aqueous solution in small, shining, anhydrous crystals, which appear to be six-sided prisms with dihedral summits. The compound has a feeble, somewhat bitter taste, not at all acid, and does not redden litmus; it fuses at a temperature just below redness.

| Calculation, according to Berzelius. | | | | Or: | | | |
|---|---|---|---|---|---|---|---|
| K | 39·2 | | 31·41 | KF | 57·9 | | 46·39 |
| B | 10·8 | | 8·65 | $BF^3$ | 66·9 | | 53·61 |
| 4F | 74·8 | | 59·94 | | | | |
| $KF, BF^3$ | 124·8 | | 100·00 | | 124·8 | | 100·00 |

When heated nearly to redness, it boils up and evolves gaseous fluoride of boron, which, if the compound is not perfectly anhydrous, condenses to small drops of hydrofluate of boracic acid: but it is only by a strong heat long continued, that the compound can be entirely resolved into volatile fluoride of boron and solid fluoride of potassium. If the decomposition is incomplete, the remaining fluoboride of potassium is left behind on dissolving the fluoride of potassium in water. Oil of vitriol decomposes this substance slowly, and only by the aid of heat; at first, gaseous fluoride of boron escapes; then aqueous hydrofluate of boracic acid and hydrofluoric acid, leaving a quantity of sulphate of potash equivalent to 37·417 per cent. of potash. The compound is not decomposed by any base, such as ammonia, potash, or soda; nor even by heating with sal-ammoniac,—though, when it contains fluoride of silicium and potassium, hydrofluosilicate of ammonia is evolved.—One part of the double fluoride of boron and potassium dissolves in 70·4 parts of cold, and in a somewhat smaller quantity of hot water. Solutions of ammonia, caustic potash and soda, and their carbonates, do not dissolve it more readily than water, and suffer it to crystallize out unchanged on cooling. If fluoride of silicium and potassium is present, ammonia decomposes it, and the purer compound crystallizes out. Fluoboride of potassium is slightly soluble also in boiling alcohol, and crystallizes out again as it cools. (Berzelius, *Pogg.* 2, 118.)

## Potassium and Nitrogen.

A. Nitride of Potassium.—Formed by heating amide of potassium to redness in a close vessel.—Greenish-black, infusible. (Gay-Lussac & Thénard). After more powerful heating, it is black, with somewhat less lustre than black-lead; opaque, very brittle, grey when powdered; does not melt at a red heat; conducts electricity. (H. Davy.)—Separates at a very high temperature into potassium and nitrogen gas; generally takes fire spontaneously in the air, and burns with a dark red flame; evolving nitrogen gas if burnt in oxygen or heated with red oxide of mercury. Effervesces violently with water, and yields potash and ammonia, with a trace of hydrogen.

$$K^3N + 3HO = 3KO + NH^3.$$

Unites with phosphorus or sulphur when heated, forming a highly inflammable mixture, which, when it comes in contact with water, evolves

phosphuretted hydrogen or sulphuretted hydrogen gas, as well as ammonia. (H. Davy.)

| | | Calculation. |
|---|---|---|
| 3K | 117·6 | 89·36 |
| N | 14·0 | 10·64 |
| $K^3N$ | 131·6 | 100·00 |

B. Amide of Potassium. *Olive-coloured compound of Potassium*, discovered by Gay-Lussac & Thénard.—Potassium gently heated in ammoniacal gas, fuses with considerable effervescence, assuming a blue, green, and ultimately an olive-green colour. The heat must then be immediately withdrawn. Potassium which separates one measure of hydrogen gas from water, causes the disappearance of nearly 2 measures of ammoniacal gas—less, however, at a higher than at a lower temperature —always setting one measure of hydrogen free. (Gay-Lussac & Thénard.) The compound is an imperfectly crystallized greenish brown mass, without metallic lustre (Gay-Lussac & Thenard), exhibiting a brown colour by transmitted light, but only when in extremely thin scales; sinks down quickly in oil of sassafras; fuses a little above 100°; does not conduct electricity. (H. Davy.)

| | | Calculation. |
|---|---|---|
| K | 39·2 | 71·02 |
| 2H | 2·0 | 3·62 |
| N | 14·0 | 25·36 |
| K, Ad | 55·2 | 100·00 |

*Decompositions.*—1. Amide of potassium effervesces at a temperature below redness, evolving scarcely anything but ammoniacal gas, and remaining green. When heated to dull redness, it evolves decomposed ammoniacal gas, *i. e.* hydrogen and nitrogen gases, in the proportion, by volume, of 3 : 1, together with undecomposed ammoniacal gas, the quantity of which continually increases; it then becomes greenish black and infusible (nitride of potassium). The whole of the gas evolved, considered as ammoniacal gas, does not quite amount to $\frac{2}{3}$ of the quantity absorbed in the formation of the amide of potassium. (Gay-Lussac & Thénard.)

$$3(K, NH^2) = K^3N + 2NH^3.$$

—2. Heated with easily fused metals, it evolves nitrogen and ammoniacal gas, with but little hydrogen; and there remains an alloy of potassium with a portion of the black substance (nitride of potassium). (Gay-Lussac & Thénard.)—3. Fused in oxygen gas, it burns with brilliant emission of sparks, evolving nitrogen and passing to the state of hydrate of potash. At a red heat, it also burns rapidly in the air. (Gay-Lussac & Thénard, H. Davy).—4. With water it forms hydrate of potash, becoming heated and often inflamed, and evolves—if an excess of water is avoided—exactly the quantity of ammoniacal gas previously decomposed by the potassium; no hydrogen is evolved unless free potassium is present. In the air, it likewise separates into ammonia and hydrate of potash. Hydrated acids and alcohol act like water. Rock-oil does not decompose it. (Gay-Lussac & Thénard, *Recherch.* 1, 337; H. Davy, *Phil. Trans.* 1809, 40 and 450.)

C. Nitrite of Potash.—1. Nitre is kept at a red heat for a long time, the mass dissolved in boiling water, and the undecomposed nitrate of potash left to crystallize out first. The mother-liquor, on further

evaporation and cooling (or by being neutralized with acetic acid and mixed with twice its volume of alcohol of 90 per cent. *Fischer, Pogg.* 77, 115), deposits crystals of the nitrite. Deiman (*Scher. J.* 7, 273) supposed that a compound of nitric oxide and potash must exist in the mother-liquor, because the irregularly crystallized mass of salt obtained on evaporating that liquid, evolved nitric oxide gas when mixed with acids; this reaction may, however, just as well proceed from nitrite of potash. For the same reason, Hess (*Pogg.* 12, 257) considered nitrite of potash as a compound of nitric oxide and potash. (See, however, II., 382.)—2. Vapour of hyponitric acid evolved by heating fuming nitric acid, or the vapour produced by heating starch with nitric acid, is passed into solution of potash. By this process, nitrate of potash is formed at the same time. (Fritzsche, *Pogg.* 39, 134.)—3. Nitrite of lead is precipitated by carbonate of potash (Berzelius), or nitrite of silver by chloride of potassium. (II. 381.)—White crystalline deliquescent salt, without alkaline reaction.

D. Nitrate of Potash.—*Saltpetre, Prismatic Saltpetre, Nitre, Potash-nitre, Nitrum.*—This salt is found in many places on the earth's surface where organic matter has been decomposed, especially in hot climates, as in India, South America, and Spain.—(For the mode of its formation, *vid.* II. 388.) Hydrate of potash emits light when sprinkled with nitric acid in the dark. (Heinrich.)

*Preparation.*—1. The earth of certain regions in the East Indies, rich in nitre, is exhausted with water, and the solution evaporated to the crystallizing point.—2. Azotized organic substances both of the vegetable and animal kingdom, after they have begun to putrefy by exposure to the air in a dark place,—are mixed with substances containing potash, lime, or magnesia, in the state of carbonates—heaped together in ridges (*saltpetre-walls*) or low pyramids (*saltpetre-mounds*)—moistened with drainings from dung-heaps, urine, &c., and exposed to the air. By exhausting this *saltpetre-earth* with water, after the lapse of months or years, the crude saltpetre-ley is obtained, containing—besides nitrate of potash—the nitrates of lime and magnesia, chloride of potassium, chloride of sodium, and organic matter, &c. From this, after sufficient evaporation, the greater part of the lime and magnesia is precipitated by carbonate of potash. (Sulphate of potash may likewise be used to throw down the lime.) The decanted liquid is evaporated to a considerable extent, whereupon the greater part of the chlorides of potassium and sodium crystallizes out and is separated mechanically. The concentrated liquid yields, on cooling in the crystallizing vessels, *raw nitre* or *saltpetre*, which, by repeated solution in hot water and recrystallization, is converted into *purified nitre.* This is further purified, on the small scale, by several recrystallizations.—Even *purified nitre* still contains chlorides. From these it may be freed by recrystallization, according to the method already described; (I., 15), or, according to Grote (*N. Br. Arch.* 15, 192), by pounding the nitre, moistening it with $\frac{1}{16}$ its weight of nitric acid and a small quantity of water in a porcelain dish, stirring all the while—evaporating the liquid to perfect dryness—and repeating the process with a smaller quantity of acid, if the salt still contains chlorine.—Or, by precipitation with nitrate of silver or subnitrate of mercury, filtering, and then decomposing the excess of metallic salt by sulphuretted hydrogen.

Nitre is dimorphous; *a.* Its ordinary form belongs to the right prismatic system. (*Fig.* 54, 55, 56, and other forms); $u : u$ backwards =

119°; $u : u^1 = 61°$; $u$ or $u^1 : t = 120\frac{1}{2}°$. Sp. gr. = 1·933. (Mattson), 2·058 (Kopp), 2·1006 (Karsten.) Large crystals crack with the warmth of the hand.—*b.* More rarely, nitre crystallizes in the obtuse flattened rhombohedrons of nitrate of soda. (*Fig.* 141), (I., 101.)—Both kinds of crystals are anhydrous.—Nitre fuses below a red heat, without loss, and contracts on cooling to a white, opaque, fibrous mass, *Nitrum tabulatum, Mineral Crystal.*—Melted in a thin layer on glass, it solidifies, on cooling, in transparent masses, consisting of but few individual crystals, which, by examination with the microscope, are observed, when touched by a needle (or after a few minutes, even of themselves) to undergo a change, commencing from the point of contact and extending through the whole mass. (Talbot, *Phil. Mag. An.* 12, 145.) [Probably a transition from the rhombohedral to the right prismatic system.]—Permanent in the air—Taste, sharp, bitter, and cooling.

| | Calculation. | Thomson. | Wollaston. | Longchamp. | Wenzel. |
|---|---|---|---|---|---|
| KO | 47·2 | 46·64 | 45·66 | 46·668 | 46·703 | 48 |
| $NO^5$ | 54·0 | 53·36 | 54·34 | 53·332 | 53·297 | 52 |
| KO, $NO^5$ | 101·2 | 100·00 | 100·00 | 100·000 | 100·000 | 100 |

| | Bérard. | Curaudau. | Berthollet. | Dalton. | Thénard. | Richter. | Laugier. |
|---|---|---|---|---|---|---|---|
| KO | 48·64 | 49·76 | 50·1 | 52·5 | 53 | 53·4 | 62 |
| $NO^5$ | 51·36 | 50·24 | 49·9 | 47·5 | 47 | 46·6 | 38 |
| | 100·00 | 100·00 | 100·0 | 100·0 | 100 | 100·0 | 100 |

At a red heat, it evolves oxygen gas, at first tolerably pure, but afterwards contaminated with a constantly increasing quantity of nitrogen, and is thereby converted first into nitrite, and then into pure potash and peroxide of potassium. Vessels of earthenware and glass, when used for this process, are corroded, in consequence of the potash dissolving out silica; and most metallic vessels become oxidized, the oxide produced uniting with the potash: silver and gold resist better than platinum. Nitre detonates in the fire with charcoal and other combustible bodies, as sulphur, phosphorus (with the latter according to Brugnatelli, even when struck with a warm hammer), iron and zinc; it even oxidizes silver, gold, and platinum. (*Vid.* II., 400.)

The following applications of nitre depend on these decompositions:

1. For the preparation of oxygen gas.

2. *Gunpowder* (a mixture of 6 parts of nitre, one part of sulphur, and one part of charcoal, or more accurately, of 101·2 parts [one At.] of nitre, 16 parts [one At.] of sulphur, and 18 parts [3 At.] of charcoal), is decomposed at an elevated temperature, with vivid combustion and explosion, into nitrogen and carbonic acid gases, which acquire at that heat a high degree of elasticity—and protosulphide of potassium, which likewise assumes the form of vapour;

$$KO, NO^5 + S + 3C = KS + N + 3CO^2.$$

An excess of carbon remains mixed with the sulphide of potassium, which, if air is present, may be partially burnt and converted into sulphate of potash.

3. *Powder of Fusion*, or Baume's *Quick-flux.* A mixture of 3 parts of nitre, one part of sulphur, and one part of sawdust, which, if set on fire in a walnut shell filled with it, burns with so much heat, that a small silver or copper coin exposed to it, is melted in a moment.

4. *Detonating-powder*, a mixture of 3 parts of nitre, 2 parts of pearl-ash, and one part of sulphur, very dry, finely mixed and slowly heated. It explodes with a very loud report, and often fractures very strong vessels. The detonation occurs according to M. Meyer (*J. pr. Chem.* 2, 110) at 164° (327·2° F.) as soon as all the sulphur is in a state of fusion, without any previous escape of carbonic acid gas. Meyer supposes that the action depends upon the sudden evolution of nitrogen and carbonic acid gas, while sulphate of potash is formed; and 3 atoms (303·6 parts) of nitre, 2 atoms (98·4 parts) of carbonate of potash, and 5 atoms (80 parts) of sulphur are concerned in it.

$$3(KO,NO^5) + 2(KO,CO^2) + 5S = 5(KO,SO^3) + 3N + 2CO^2.$$

5. *Lucifer Matches:* 9 parts of phosphorus, 14 parts of nitre, 16 parts of finely powdered manganese or red lead, and 16 parts of gum-arabic; for a description of the process *vid.* Böttger (*Ann. Pharm.* 37, 113). Other mixtures of this kind contain also sulphur, chlorate of potash, nitrate of lead, peroxide of lead, &c.

Nitre dissolves in water, producing great cold. One part dissolves at 0° in 13·32, at 18° in 3·45, at 45° in 1·34, and at 97° in 0·424 parts of water (Gay-Lussac); it dissolves at 18° in 3·4 parts of water, forming a liquid of specific gravity = 1·1601 (Karsten); in 3·62 parts of water at 18°, forming a liquid of specific gravity = 1·151 (Longchamp); it dissolves in 4 parts of water at 16°, in $\frac{1}{4}$ part of boiling water, and in 100 parts of alcohol. (Riffault.) The presence of nitrate of lime or common salt in the water enables it to dissolve a much larger quantity of nitre. (Lemerg, Vauquelin, Longchamp, *Ann. Chim. Phys.* 9, 5.)

Powdered nitre absorbs the vapour of anhydrous sulphuric acid abundantly at ordinary temperatures, and is converted into a greasy mass which afterwards hardens, and, if heated or kept for some time, evolves vapour of nitrous acid. (H. Rose, *Pogg.* 38, 122.)

E. Boro-nitride of Potassium?—A mixture of 7 parts (2 At.) of vitrefied boracic acid and 20 parts (3 At.) of dry cyanide of potassium kept at a white heat for an hour in a covered charcoal crucible, yields a white, porous, brittle, infusible mass, insoluble in water, hydrated acids, or alkalis, even when boiled,—not decomposed at a red-heat, either by chlorine gas, or by potassium, or other metals,—but evolving ammonia in abundance if heated in contact with steam or hydrate of potash, and detonating when thrown on chlorate or nitrate of potash in a state of fusion.

$$2BO^3 + 3(K,NC^2) = K^3N^3B^2 + 6CO.$$

(Balmain, *Phil. Mag. J.* 21, 270.)

F. Sulphite of Nitric Oxide and Potash.—1. An aqueous solution of potash completely absorbs a mixture of 2 measures of nitric oxide and one measure of sulphurous acid gas.—2. Nitric oxide gas is passed through a solution of sulphite of potash mixed with potash and contained in a Woulfe's apparatus.—Colourless, irregular, six-sided prisms, similar to those of nitre; inodorous, bitter, and neutral. Remains unaltered at 115°; decomposed at 130° into nitric oxide gas and sulphite of potash. All acids, even the weakest, as well as spongy platinum, oxide of silver, chloride of barium, manganous sulphate, oxide of copper or zinc, and

acetate of lead, decompose this potash salt,—though more slowly than the corresponding salt of ammonia—into 20 per cent. of nitrous oxide, and 80 per cent. of sulphate of potash. It dissolves very readily in water, and is decomposed in solution, even by a slight elevation of temperature; insoluble in alcohol. (Pelouze, *Ann. Chim. Phys.* 60, 160.)

| | | Crystallized. | |
|---|---|---|---|
| KO | 47·2 | | 43·22 |
| $NO^2$ | 30·0 | | 27·47 |
| $SO^2$ | 32·0 | | 29·31 |
| $KO, NO^2, SO^2$ | 109·2 | | 100·00 |

¶ G. Pyrophosphate of Potash and Ammonia.—Prepared by saturating acid pyrophosphate of potash with ammonia, and evaporating the solution over a mixture of burnt lime and sal-ammoniac. White deliquescent salt. Its solution has an alkaline action, and evolves ammonia when boiled—being converted into acid phosphate of potash. Nitrate of silver precipitates it white, and the supernatant liquid is acid to test paper.

| | Calculation. | | Schwarzenberg. |
|---|---|---|---|
| 2KO | 94·4 | 33·56 | 33·65 |
| $NH^3$ | 17·0 | 6·04 | 6·61 |
| $2PO^5$ | 142·8 | 50·80 | 50·41 |
| 3HO | 27·0 | 9·60 | 9·33 |
| $2KO, PO^5 + NH^4O, HO, PO^5 + Aq.$ | 281·2 | 100·00 | 100·00 |

(A. Schwarzenberg, *Ann. Pharm.* 65, 2.) ¶.

H. Sulphate of Potash and Ammonia.—Scaly, shining, bitter crystals, unacted on by the air, and leaving neutral sulphate of potash when ignited. (Link, *Orell. Ann.* 1796, 1, 29.)

## Potassium and Potassium.

A. Bisulphate of Potash with Biniodate of Potash.—$KO, 2SO^3 + KO, 2IO^5$—The mother-liquor of biniodate of potash (III., 52) yields this compound, on further evaporation, in transparent crystals which contain 46·8 per cent. of iodine, and when heated to redness, leave 18·36 per cent. of sulphate of potash, evolving oxygen gas and vapour of iodine. If the solution in water is left to evaporate spontaneously, biniodate of potash crystallizes out, leaving the bisulphate in the mother-liquor. (Serullas, *Ann. Chim. Phys.* 43, 117.)

B. Chloride of Potassium and Carbonate of Potash in atomic proportions heated over the spirit-lamp, melt to a clear thin liquid, which, as it cools, solidifies to a white, scaly mass, and if heated to redness with boracic acid, yields carbonic acid, but no phosgene gas. (Döbereiner, *Pogg.* 55, 240.)

C. Chloride of Potassium and Sulphate of Potash in atomic proportions fuse very easily to a clear liquid, which yields, on cooling, a homogeneous, translucent—sometimes fibrous, sometimes granular mass. (Döbereiner.)

D. Chloride of Potassium with Biniodate of Potash.—1. An aqueous solution of terchloride of iodine is mixed, not quite to saturation, with caustic potash or carbonate of potash, and the liquid left to evaporate spontaneously. (Serullas.) Probably thus:—

$$KO + 4ICl^3 + 10HO = KO, 2IO^5 + 2ICl + 10HCl.$$

The addition of potash to chloride of iodine causes a precipitation of iodine, which, however, redissolves immediately as long as the liquid remains acid; if it be left in this condition, the pure compound crystallizes out; but by a greater concentration of the solution, it becomes mixed with more or less of the double chloride of iodine and potassium; if hydrochloric acid is added to the solution, crystals of this compound alone are produced. (Filhol.)—2. Hydrochloric acid is heated with iodate of potash. (Serullas.)

$$2(KO, IO^5) + HCl = KCl + KO, 2IO^5 + HO.$$

The hydrochloric acid must be diluted with 12 times its volume of water, in which case no chlorine is evolved and no double chloride of iodine and potassium formed. (Filhol.) When a solution of chloride of potassium and biniodate of potash is evaporated, the latter salt crystallizes out by itself; the presence of free hydrochloric acid is necessary to the formation of this compound. (Serullas.) Brilliant, transparent, colourless prisms, and elongated four-sided tables with truncated terminal edges; it reddens litmus.

Calculation, according to Serullas.

| | | | |
|---|---|---|---|
| KCl | 74·6 | | 16·44 |
| KO, $2IO^5$ | 379·2 | | 83·56 |
| KCl + KO, $2IO^5$ | 453·8 | | 100·00 |

100 parts of the salt contain 54·2 parts of iodine and 7·396 parts of chlorine. (Serullas.) The crystals effloresce in the air. The salt on being heated to redness, leaves 66 per cent. of iodide of potassium mixed with a small quantity of chloride. It is soluble in 19 parts of water at 15°. (Serullas, *Ann. Chim. Phys.* 43, 121.) As the compound, when treated with cold alcohol, leaves chloride of potassium, it is probably a mere mixture of the two salts. (Filhol, *J. Pharm.* 25, 506.)

## Other Compounds of Potassium.

With many metals, as with sodium, arsenic, antimony, tellurium, bismuth, zinc, tin, lead, iron, mercury, and platinum. These compounds are obtained, sometimes by galvanic action, sometimes by the immediate contact of potassium with the metals or their oxides, sometimes again by the ignition of a mixture of charcoal and carbonate of potash, (*e. g.* carbonized tartar) with the metal in a state of fine division. (Vauquelin, *Ann. Chim. Phys.* 7, 32; also *N. Tr.* 3, 1, 282; Serullas, *J. Pharm.* 6, 571; *J. Phys.* 91, 123; 93, 115.) The potassium in most of these alloys is rapidly oxidized by the oxygen of the air and of water; many of them, when placed on mercury covered with a thin stratum of water, assume a continuous rotatory motion which goes on till the potassium is completely oxidized. (l., 81.)

CHAPTER II.

# SODIUM.

*Natron-metall, Natronium, Natrium.*

*History.* From soda—which was formerly confounded with potash, but proved to be a distinct substance by Duhamel in 1736, and subsequently by Marggraf in 1758—Sir H. Davy first obtained this metal in the year 1807.

*Sources.* As chloride of sodium, in rock-salt, sea-water, salt-springs, many mineral waters and springs; rarely, as carbonate, borate, and sulphate of soda, either in springs, lakes, &c., or in the solid state; abundantly, as nitrate of soda; further in Glauberite, Gay-Lussite, kryolite; and in combination with silica and other earths in chabasite, analcime, natrolite, Thomsonite, eudialite, albite, soda-spodumene, labrador, nepheline, hauyne, sodalite, brewicite, cancrinite, and achmite; in very small quantity also in bole, pitchstone, pumice-stone, obsidian, ittnerite, and pinite; traces of soda-salts are also found in coal, in all kinds of limestone and dolomite, in talc, asbestos, emerald, manganese, red hæmatite, native molybdate of lead and sulphide of antimony. (Kuhlmann, *Ann. Pharm*, 41, 220; A. Vogel. *J. pr. Chem.* 25, 230.) In the vegetable kingdom it occurs as sulphate, hydriodate, and hydrochlorate of soda, and combined with vegetable acids, especially in plants growing in or near the sea; in the animal kingdom, combined with carbonic, phosphoric, sulphuric, hydrochloric, and various organic acids.

*Preparation.* Similar to that of potassium.—1. By electricity. The decomposition of hydrate of soda is more difficult than that of hydrate of potash. (H. Davy.)—2. From hydrate of soda and iron at a white-heat. Sodium being less volatile than potassium, Gay-Lussac & Thénard (*Recherch.* 1, 97) employ in their process hydrate of soda with which a very small quantity of hydrate of potash is mixed, and separate the potassium from the resulting alloy by keeping it in thin plates, under rock-oil in vessels not completely closed: under these circumstances, the potassium oxidizes first.—3. From carbonate of soda and charcoal in the mercury-bottle. The preparation of sodium by this method is easier than that of potassium. Since sulphate of soda, if mixed with the carbonate, becomes reduced to sulphide of sodium, which acts on the iron-bottle, it is necessary to use pure carbonate of soda, such as is obtained by the ignition of acetate of soda. When the quantity of charcoal is too small, the mass fuses, spirts into the tube, and chokes it up. 1 lb. of dry finely-divided carbonate of soda intimately mixed with ¼ lb. of fine charcoal powder, and then with ½ lb. of charcoal in coarser grains, yields 4½ oz. of sodium, with very little black residue, and without stopping up the tube in the least. (Schädler, *Ann. Pharm. 20, 2.*) 66 oz. of crystallized carbonate of

soda may also be heated to dryness in an iron vessel, stirring all the while, with 6 oz. of finely-divided charcoal, and 12 oz. of coarse charcoal powder added to the pulverulent mass. (Gmelin.) To purify the globules of sodium, Schädler ties them up in strong and not very fine linen, heats them in rock-oil to the boiling point, and presses out the sodium which then runs together.

*Properties.* Silver-white, with a high lustre. Sp. gr. = 0·9348 (H. Davy), 0·97223 at 15° (Gay-Lussac & Thénard); crystallizes in cubes (Schädler). Recently cut sodium put into oil of turpentine exhibits crystalline markings on the cut surfaces. (Böttger.) At − 20° it is rather hard; at 0°, very ductile; at ordinary temperatures, of the consistence of wax; at 50°, semi-fluid; at 90°, perfectly so. Less volatile than potassium, according to Sir H. Davy, and also Gay-Lassac & Thénard; but according to Mitscherlich (*Pogg.* 29, 230), somewhat more so. Vapour of sodium is colourless. Sodium is an excellent conductor of heat and electricity. (H. Davy.)

Atomic weight of sodium, 22·97. (Pelouze, *Compt. Rend.* 20, 1047.)

## *Compounds of Sodium.*

### Sodium and Oxygen.

### A. Suboxide of Sodium.

This compound is obtained in the same manner as suboxide of potassium. Dark grey (H. Davy), greyish-white (Gay-Lussac & Thénard), dull, brittle mass; more combustible than sodium. Decomposes water.

### B. Soda. NaO.

*Protoxide of Sodium, Mineral Alkali, Soude, Natrum, Natron.*

*Formation.*—1. By burning sodium in dry air or oxygen gas at a very high temperature. (H. Davy.) Sodium requires a much greater heat than potassium to make it burn rapidly, but it then burns like potassium, with white light and emission of sparks. (H. Davy.) It does not oxidize at ordinary temperatures in perfectly dry air. (Bonsdorff, *Pogg.* 41, 296.)

2. Sodium dissolves rapidly in water, out of contact of air, forming a solution of soda, with great evolution of heat and hydrogen gas. It gradually oxidizes in the air by decomposing a part of its water and absorbing another portion to form hydrate of soda, which forms a crust round the remaining metal. Thrown on water exposed to the air, it swims about, presenting the appearance of a silvery, fused, constantly decreasing globule, and producing a constant hissing from the escape of hydrogen gas, till the whole is dissolved as soda.—Sodium, in decomposing water, seems to produce less heat, or requires a higher temperature to inflame it, than potassium; for the cooling effect of the mass of water prevents the production of sufficient heat to cause combustion. Sodium does not take fire on a moistened metallic surface—with difficulty on

wet glass—easily on moistened paper or wood, however, and still more so on damp charcoal or a thick solution of gum. (H. Davy; Ducatel, *Sill. Amer. J.* 25, 90; Serullas, *Ann. Chim. Phys.* 40, 329.) The smaller the conducting power of the surface on which it rests, the more easily does the sodium inflame. When thrown upon hot water, it emits sparks, in consequence of pieces of the metal being thrown off and taking fire in the air. (H. Davy.) It takes fire on water above 40°, and burns with a brighter flame than potassium. (Balcells, *J. Chim. Med.* 3, 21.) It takes fire at ordinary temperatures on concentrated phosphorous, phosphoric, sulphurous, sulphuric (either pure, or mixed with not more than 6 times its bulk of water), hydrofluoric, hyponitric, nitric, and arsenic acids, though it appears in every case to decompose nothing but the water; on concentrated hydrochloric, oxalic, or acetic acid, it does not take fire. (Gay-Lussac & Thénard.) If the globule of sodium, whilst revolving in the water in a state of fusion, be struck with a flat spatula, a report follows, attended with splashing of the water, and occasionally with fracture of the vessel (Wagner), the sodium being scattered over the water in fine globules by the blow, and a considerable quantity of hydrogen gas being thus set free at the same moment. (Couerbe, *J. Pharm.* 19, 224.)

3. Sodium like potassium decomposes—though generally only on elevation of temperature, and with less powerful combustion—carbonic acid and carbonic oxide, boracic acid, phosphoric acid, hyponitric acid (not vapour of nitric acid), arsenious, arsenic, chromic, molybdic, and hydrocyanic acids; likewise, the oxides of the heavy metals, namely: the oxides of chromium, manganese, cobalt, antimony, bismuth, zinc, tin, lead, iron, nickel, copper, mercury, silver, and platinum; and in every case but that of chromium and manganese, the metal itself is plainly reduced;—lastly, it decomposes the salts of carbonic, sulphuric, nitric acids, &c., and deoxidizes, not only the acid, but the base also, if it happens to be the oxide of a heavy metal. (Gay-Lussac & Thénard.)

*Preparation.* By burning sodium at a high temperature; or by methods similar to those described for the preparation of potash.

*Properties.* Grey mass having a conchoidal fracture; fusing at a strong red heat; volatilized with difficulty; a non-conductor of electricity. (H. Davy.) Soda, obtained by heating sodium with hydrate of soda, has a specific gravity of about 2·805. (Karsten.) Acts like potash on vegetable colours and organic matter, but is somewhat less corrosive.

| | Calculation. | | Berzelius. | H. Davy. | Gay-Lussac & Thénard. |
|---|---|---|---|---|---|
| Na | 23·2 | 74·36 | 74·3383 | 74·6 | 74·7 |
| O | 8·0 | 25·64 | 25·6617 | 25·4 | 25·3 |
| Na, O | 31·2 | 100·00 | 100·0000 | 100·0 | 100·0 |

(NaO = 290·9 + 100 = 390·9. Berzelius.)

*Decompositions.* Similar to those of potash.

*Combinations.—a.* With water.

*a. Hydrate of soda—Soda-caustic.* Soda mixed with a little water, passes into the state of hydrate, with great evolution of heat.—*Preparation:* similar to that of potash:—1. From carbonate of soda and lime. To a

boiling solution of 3 parts of crystallized carbonate of soda in 15 parts water or more, a quantity of cream of lime prepared by slaking one part of lime with three parts water, is added by small portions at a time, the whole boiled for some time, and treated as for potash. Soda yields its carbonic acid to lime more readily than potash. Purification by alcohol may also be applied in this case.—2. By precipitating sulphate of soda with baryta-water. The process is similar to that for the preparation of potash. The tests of purity are also the same.

White, opaque, brittle substance, of a fibrous texture; sp. gr. =2·00. (Dalton.) Fuses below redness, but is less volatile at a red heat than hydrate of potash. Hydrate of soda on platinum wire colours the blow-pipe-flame intensely yellow, even if mixed with a large quantity of potash. It is not precipated in solution by perchloric acid, sulphate of alumina, or chloride of platinum, nor—unless highly concentrated—by carbazotic and tartaric acids.

| | Calculation. | | Berard. | H. Davy. | Gay-Lussac & Thénard. | Darcet. |
|---|---|---|---|---|---|---|
| NaO ..... | 31·2 .... | 77·61 .... | 81·14 .... | 77·8 .... | 76·11 — 73·85 .... | 72 |
| HO..... | 9·0 .... | 22·39 .... | 18·86 .... | 22·2 .... | 23·89 — 26·15 .... | 28 |
| NaO, HO | 40·2 .... | 100·00 .... | 100·00 .... | 100·0 .... | 100·00 „ 100·00 .... | 100 |

*β. Crystallized Soda.*—Soda crystallizes—only however by great reduction of temperature—from an aqueous solution, in colourless, four-sided tables which are very fusible.

*γ. Solution of Soda.—Liquid Soda, Soda-ley, Caustic-ley, Soap-boilers' ley.* Soda, hydrate of soda, and crystallized soda, deliquesce in the air till they are converted into carbonate. The first two dissolve in water with evolution—the crystals with absorption of heat. Solution of soda is obtained in the same manner as solution of potash. It is a colourless caustic liquid. A solution saturated at common temperatures has a specific gravity of 1·500, according to Dalton; boils at 130° (266° F.), and contains 36·8 per cent. of soda. 100 parts of water dissolve, at 18° (64·4° F.), 60·53 parts of hydrate or 41·43 parts of dry soda; at 32° (89·6° F.) 72·91 hydrate or 45·72 soda; at 55° (131° F.) 100 hydrate or 63·53 soda; at 70° (158° F.) 116·75 hydrate or 71·98 soda; and at 80° (176° F.) 127·02 hydrate or 78·3 soda. (Osann.)

*Quantity of Soda in a Solution of Soda at* 15° (59° F.) *according to Tünnermann.* (*N. Tr.* 18, 2, 11.)

| Sp. gr. | Per cent. | Sp. gr. | Per cent. | Sp. gr. | Per cent. | Sp. gr. | Per cent. |
|---|---|---|---|---|---|---|---|
| 1·4285 | 30·220 | 1·3198 | 22·363 | 1·2392 | 15·110 | 1·1042 | 7·253 |
| 1·4193 | 29·616 | 1·3143 | 21·894 | 1·2280 | 14·506 | 1·0948 | 6·648 |
| 1·4101 | 29·011 | 1·3125 | 21·758 | 1·2178 | 13·901 | 1·0855 | 6·044 |
| 1·4011 | 28·407 | 1·3053 | 21·154 | 1·2058 | 13·297 | 1·0764 | 5·440 |
| 1·3923 | 27·802 | 1·2982 | 20·550 | 1·1948 | 12·692 | 1·0675 | 4·835 |
| 1·3836 | 27·200 | 1·2912 | 19·945 | 1·1841 | 12·088 | 1·0587 | 4·231 |
| 1·3751 | 26·594 | 1·2843 | 19·341 | 1·1734 | 11·484 | 1·0500 | 3·626 |
| 1·3668 | 25·989 | 1·2775 | 18·730 | 1·1630 | 10·879 | 1·0414 | 3·022 |
| 1·3586 | 25·385 | 1·2708 | 18·132 | 1·1528 | 10·275 | 1·0330 | 2·418 |
| 1·3505 | 24·780 | 1·2642 | 17·528 | 1·1428 | 9·670 | 1·0246 | 1·813 |
| 1·3426 | 24·176 | 1·2578 | 16·923 | 1·1330 | 9·066 | 1·0163 | 1·209 |
| 1·3349 | 23·572 | 1·2515 | 16·319 | 1·1233 | 8·462 | 1·0081 | 0·604 |
| 1·3273 | 22·967 | 1·2453 | 15·714 | 1·1137 | 7·857 | 1·0040 | 0·302 |

(Richter's Tables, *Stöchiometrie*, 3, 332; Dalton's Elements, 2, 315.)

*b.* With acids, forming the SODA-SALTS. The affinity of soda for all acids is somewhat less than that of potash. The soda-salts are colourless unless the acid itself is coloured; they are for the most part fixed in the fire. Attached to a platinum wire in the blow-pipe flame, they give a strong yellow colour, which is not destroyed but merely weakened, if they are mixed with even 20 or 30 times their weight of a salt of potash. The flame of alcohol when heated with them, is also coloured yellow. The salts of soda are much more disposed than the corresponding salts of potash to unite with a large quantity of water of crystallization, and thus form efflorescent salts (*e. g.* sulphate of soda and sulphate of potash). Nearly all soda-salts dissolve readily in water. The solution is not precipitated by perchloric acid, sulphate of alumina or bichloride of platinum, nor, when sufficiently diluted, either by tartaric or carbazotic acids. With hydrofluosilicic acid they yield a gelatinous precipitate. This, when viewed under the microscope, is seen to consist of six-sided crystals, whereas that obtained with salts of potash is gelatinous and amorphous. (Harting, *J. pr. Chem.* 22, 50.) Soda forms double salts, especially with the salifiable bases already enumerated under the head of potash.

*c.* With the earths, soda forms compounds similar to those of potash.

*d.* Also with the oxides of the heavy metals mentioned under potash.

*e.* Also with various organic substances.

## C. PEROXIDE OF SODIUM.

*Formation.*—1. By burning sodium in dry air or oxygen gas, on a piece of platinum or silver fused over with common salt, the heat being applied—not too strongly—from without.—2. By heating to redness soda or hydrate of soda in contact with air or oxygen gas, or by the ignition of nitrate of soda.

*Properties.* Dirty greenish yellow substance, less fusible than hydrate of soda or peroxide of potassium, and a non-conductor of electricity. When sodium is converted into peroxide by burning, it unites with $1\frac{1}{2}$ atoms of oxygen, according to Sir H. Davy; with a somewhat larger quantity, according to Gay-Lussac & Thénard. Millon (*J. pr. Chem.* 18, 293) is of opinion that the peroxide contains 2 atoms of oxygen. From the great analogy between potassium and sodium, it may be supposed that pure peroxide of sodium contains 3 atoms of oxygen; as yet, however, it has only been obtained mixed with soda.

*Decompositions.*—1. By water, into oxygen gas and solution of soda; by carbonic acid gas, with great elevation of temperature, into oxygen gas and carbonate of soda.—2. It is decomposed without inflammation, when strongly heated with charcoal or tin; and with violent inflammation, when heated with phosphorous or sulphurous acid gas; in the latter case, sulphide of sodium and sulphate of soda are formed. (Gay-Lussac & Thénard.)

## Sodium and Carbon.

### Carbonate of Soda.

*a.* Monocarbonate.—*Berthollet's Basic Carbonate of Soda, Soda, Mild Mineral Alkali, Alkali minerale fixum.*—Found in the soda lakes of Egypt, Hungary—where it effloresces on the soil, &c.; effloresces abundantly on walls. The salt found on the walls in the towns of Flanders, consists of carbonate and sulphate of soda, and is derived partly from the soda-salts in the limestone used in the preparation of the mortar, and partly from soda contained in the coal with which this limestone has been burned. (Kuhlmann, *Ann. Pharm.* 38, 42.) Sulphate of soda mixed with a small quantity of carbonate effloresces on walls in Bavaria. (A. Vogel, *J. pr. Chem.* 25, 230.)

*Preparation.*—1. By simple collection. In Egypt, in the desert of Thaiat in the western Delta, there is a pit four leagues long and a quarter of a league wide, which, during the winter months, becomes filled to the height of six feet with violet-coloured water; on the evaporation of this water, carbonate of soda remains and is loosened with iron poles. The residue is contaminated with 36 per cent. of common salt and 16 per cent. of sulphate of soda, besides sand; but after the purification to which it is subsequently submitted, only 10 per cent. of sand, 4 of common salt, and 1 of sulphate of soda. The carbonate of soda contains rather more than one, but less than $1\frac{1}{2}$ atoms of carbonic acid. (Pontet, *J. Chim. Med.* 6, 197.)—In Hungary, at Shegedin in Little Cumania, carbonate of soda effloresces on the ground. It is gathered before sunrise; the grey powder dissolved out by water; the solution thus obtained evaporated to dryness; and the residue heated to redness to destroy organic matter. The mass contains sulphate of soda and common salt mixed with the carbonate. (A. Werner, *J. pr. Chem.* 13, 126.)

2. *Native Soda*, the *Barilla* of Spain, *Blanquette* at Aiguemortes and Frontignan, *Salicor* at Narbonne, *Varec* in Brittany and Normandy, *Kelp* in Scotland; the ashes of plants growing in and close to the sea, generally prepared by burning them in trenches. Sea-shore plants: Various species of *Salsola, Salicornia, Atriplex, Statice, Batis, Mesembryanthemum, Chenopodium, Triglochin, Reaumuria*, &c. Sea-plants: Various species of *Fucus*. The soluble portion of the ash contains carbonate, sulphate, and hyposulphite of soda, sulphide, iodide, bromide, chloride, and ferrocyanide of sodium, and frequently also the corresponding compounds of potassium; the insoluble part contains carbonate and phosphate of lime, sulphide of calcium, magnesia, alumina, silica, sulphide of iron, and charcoal. The soda is combined with vegetable acids in these plants, and becomes converted into carbonate by combustion; it is originally derived from the common salt present in the soil or the sea-water. The ash of sea-plants is much poorer in carbonate of soda, and contains a much larger quantity of salts of potash than that of plants growing on the shore. According to Lampadius, soda from Alicant contains 26, Silician soda 23, that from Narbonne 14, Norwegian kelp 6, and Scottish kelp only 3 per cent. of anhydrous carbonate of soda. By exhausting the soda with water and evaporating the liquid, crystallized carbonate is obtained, and is purified by repeated crystallization.

3. *Artificial Soda.* A mixture of two parts of dry sulphate of soda, 2 parts of carbonate of lime (chalk or limestone) and one part of charcoal, is heated to redness in a reverberatory furnace, the fused mass being constantly stirred with an iron rod. (Leblanc, Dizé.) The sulphate of soda is reduced by the charcoal to the state of sulphide of sodium, with evolution of carbonic oxide gas; and the sulphide of sodium is converted by the carbonate of lime into sulphide of calcium—which, by taking up free lime, becomes insoluble—and carbonate of soda.

$$3(CaO, CO^2) + 2(NaO, SO^3) + 9C = CaO, 2CaS + 2(NaO, CO^2) + 10CO.$$

Part of the carbonic acid, however, escapes from the carbonate of lime, so that the mass, besides carbonate of soda, contains a variable but always large amount of caustic soda. The addition of manganese—recommended by some for the purpose of forming carbonic acid by oxidizing the excess of charcoal—may, at the same time, reconvert the sulphur of the sulphide of calcium into sulphuric acid. To obtain the pure carbonate from this artificial soda, it is exhausted by water; the solution boiled down in leaden pans; and the carbonate of soda with one atom of water, which precipitates in the form of flowers of soda (*Natron-mehl*), taken out of the liquid as it solidifies. The mother-liquor contains caustic soda, which, by different methods—*e. g.* evaporating and heating to redness with saw-dust—is again converted into carbonate.

4. *Other modes of preparing carbonate of soda from the sulphate.*—*a.* 100 parts of anhydrous sulphate of soda are heated to redness with 20 parts of charcoal; to the sulphide of sodium thus produced, 20 parts of iron turnings are added; then 8 parts of charcoal, then 12·5 parts of iron, and lastly 3 parts of charcoal; and the mixture of sulphide of iron and caustic soda thus obtained, is exposed to the air to absorb carbonic acid. (Alban.)—*b.* Sulphate of soda is converted into sulphide of sodium, by heating it to redness with $\frac{1}{8}$ of its weight of charcoal in a crucible; the sulphide is dissolved in water—converted, by boiling with oxide of copper, into sulphide of copper and soda-ley; the solution decanted and evaporated, in order that any undecomposed sulphate of soda may crystallize out; and the remaining liquid mixed with charcoal powder and evaporated to dryness: the residue is then heated to redness and exhausted with water, and the solution left to crystallize. (Prückner, *Schw.* 67, 102 and 113.)—*c.* Through an aqueous solution of sulphide of sodium obtained in the same manner, carbonic acid is passed till sulphuretted hydrogen ceases to be evolved. (Gren.)—*d.* The sulphide of sodium is converted into acetate of soda by means of pyroligneous acid—then evaporated and heated to redness. (Marggraf.)—*e.* Sulphate of soda dissolved in water is decomposed by acetate of lime; filtered; evaporated to dryness; and raised to a red heat. (Lampadius.)—*f.* Man decomposes sulphate of soda with carbonate of potash; the sulphate of potash crystallizes out first, and afterwards the carbonate of soda. (Hagen.)—*g.* An aqueous solution of sulphate of soda is stirred up in the cold with carbonate of baryta—then filtered and evaporated. (Kölreuter.)

5. *From common salt.*—*a.* One part (1 At.) of common-salt, dissolved in 8 parts of water, is digested with 4, or sometimes with 7·4 parts (4 At.) of powdered litharge; a bulky white mass of tetrachloride of lead is formed, and the liquid is found to contain caustic soda. (Scheele, Chaptal.)—*b.* When a moistened mixture of common salt and slaked lime is placed in a cellar, a small quantity of carbonate of soda effloresces

out. (Scheele.)—*c.* When carbonate of potash is dissolved in water together with common salt, and the solution evaporated, crystals of chloride of potassium separate from it first, and carbonate of soda afterwards.

¶ Bodo Unger, in an elaborate paper (*Ann. Pharm.* 66, 240; 67, 78) on the preparation of carbonate of soda, gives the following minute analysis of raw soda prepared from sulphate of soda, lime, and charcoal: the analyses of *soude salée, sal de Varec raffiné* by Girardin, are added for the sake of comparison.

| | Bodo Unger. | | Girardin. | | |
|---|---|---|---|---|---|
| | | Soude Salée. | Rouen. | | Havre. |
| $NaO, SO^3$ | 1·99 | 46·90 | 23·91 | | 65·0 |
| NaCl | 2·54 | 23·19 | 16·94 | | 2·0 |
| $NaOCO^2$ | 23·57 | | | NaS | 30·0 |
| NaOHO | 11·12 | | | | |
| $CaOCO^2$ | 12·90 | | | | |
| 3CaS, CaO | 34·76 | CaS 20·41 | 52·15 | | |
| FeS | 2·45 | | | | |
| $MgO, SiO^2$ | 4·74 | | | | |
| Charcoal | 1·59 | | | | |
| Sand | 2·02 | 8·40 | 6·00 | | 3·0 |
| Water | 2·10 | 1·10 | 1·00 | | |
| | 99·78 | 100·00 | 100·00 | | 100·0¶ |

*Purification of Carbonate of Soda.*—By repeated re-crystallization. Gay-Lussac (*Ann. Chim. Phys.* 55, 221; Ausz, *Ann. Pharm.* 12, 15), washes the ordinary commercial crystals with cold water; dissolves them in hot water; and cools the solution rapidly by surrounding it with cold water, stirring it all the time with a spatula, so that small crystals may be formed: these he collects on a funnel; and, after the mother-liquor has drained off, washes them with cold water till the drainings mixed with excess of nitric acid no longer give a precipitate with nitrate of silver.

*Impurities:—Sulphide of Sodium:* evolves sulphuretted hydrogen with acids. *Hyposulphite of Soda:* Hydrochloric acid liberates sulphurous acid and gradually precipitates sulphur.—*Sulphate of Soda:* Precipitate with chloride of barium and excess of dilute hydrochloric acid.—*Common Salt:* Precipitate with nitrate of oxide of silver and excess of nitric acid. *Ferro-cyanide of Sodium:* Blue or green colour on the addition of a ferroso-ferric salt, and then hydrochloric acid in excess.—*Salts of Potash:* See the reactions of these (III., 15).—*Carbonate of Lime:* This salt dissolves in water containing carbonate of soda, and remains mixed with it even after frequent recrystallization. The solution cooled down to 0°, deposits a compound of carbonate of soda and carbonate of lime in the form of a white crystalline powder, but still retains a portion of lime, which gives a cloud with oxalic acid. (Bauer, *Pogg.* 24, 367.)—*Carbonate of Magnesia* is sometimes mixed with it in the same manner. (Buchner, *Repert.* 57, 373.)

For the quantitative examination of soda, *vid.* Gay-Lussac & Welter. (*Ann. Chim. Phys.* 13, 212; also *N. Tr.* 5, 1, 124; also Fresenius & Will, *Ann. Pharm.* 47, 87.)

Carbonate of soda dehydrated by heat is white, translucent, of specific gravity 2·4659 (Karsten); fuses at a moderate red heat more readily than carbonate of potash; has an alkaline taste and reaction; but is even less caustic than carbonate of potash.

| | Calculation. | | Berzelius. | Schafgotsch. | Ure. |
|---|---|---|---|---|---|
| NaO | 31·2 | 58·64 | 58·757 | 58·65 | 59·14 |
| $CO^2$ | 22·0 | 41·36 | 41·243 | 41·35 | 40·86 |
| $NaO, CO^2$ | 53·2 | 100·00 | 100·000 | 100·00 | 100·00 |

| | Dalton. | Kirwan. | Bérard. |
|---|---|---|---|
| NaO | 59·6 | 59·86 | 62·53 |
| $CO^2$ | 40·4 | 40·05 | 37·47 |
| | 100·0 | 99·91 | 100·00 |

It is decomposed, like carbonate of potash, by steam, charcoal, and silicium.

*Combinations with Water.*—The anhydrous salt becomes heated by contact with water.

α. *Carbonate of Soda with one Atom of Water.*—1. Crystallizes on evaporating a saturated aqueous solution between 25° and 37° (Haidinger), or from the hydrate with 10 atoms of water when it has been kept in solution for some time in its own water of crystallization (Haidinger), or evaporated between 75° and 87°. (Schindler.)—2. It remains as an efflorescd mass when the salt ε is exposed to the air at a temperature of 37·5°. (Schindler.) Obtained by the first method, in four-sided tables. (Haidinger, *Pogg.* 6, 87.) It does not melt when heated, but loses its water between 87° and 100°, and forms a fine powder. At a temperature of 12·5° in dry weather, it absorbs from the air enough water to raise the per centage to 46; in moist air it absorbs still more, but not sufficient to constitute 8 atoms. It attracts carbonic acid from warm air, and is thereby partly converted into sesquicarbonate. (Schindler, *Mag. Pharm.* 33, 14.)

| | Calculation. | | Schindler, 1. | 2. | Haidinger, 1. |
|---|---|---|---|---|---|
| $NaO, CO^2$ | 53·2 | 85·53 | 85·51 | 85.55 | 82·26 |
| HO | 9·0 | 14·47 | 14·49 | 14·45 | 17·74 |
| $NaO, CO^2$ + Aq. | 62·2 | 100·00 | 100·00 | 100·00 | 100·00 |

If the salt obtained by the first method be dried at 37·5°, between bibulous paper, without first reducing it to powder, the mother-liquor still adheres to it; and as Haidinger did not remove this, he found too large a quantity of water. (Schindler.)

β. *With 5 Atoms of Water.*—1. The salt ε, exposed to the air at 12·5° is converted by efflorescence into the salt β. (Schindler.)—2. If the salt ε be melted and the soluble part poured off, the salt β crystallizes out at a temperature above 33°. (Berzelius.)—3. Accidentally obtained at the Buxweiler soda-works in transparent rhombic octohedrons, which effloresced slightly in the air, and when dissolved in water and evaporated at 30°, again yielded the same salt. (Persoz, *Pogg.* 32, 303; also *J. pr. Chem.* 3, 49.)

| | Calculation. | | Persoz, 3. |
|---|---|---|---|
| $NaO, CO^2$ | 53·2 | 54·18 | 53·25 |
| 5HO | 45·0 | 45·82 | 46·75 |
| $NaO, CO^2$ + 5Aq. | 98·2 | 100·00 | 100·00 |

γ. *With 6 Atoms of Water.*—Crystallizes from a solution of protosulphide of sodium exposed to the air, and frequently also from a mixed

aqueous solution of carbonate of potash and common salt. (Mitscherlich, *Pogg.* 8, 441.)

*δ. With* 8 *Atoms of Water.*—Crystallizes out when the salt ε cools from a state of fusion or from a hot saturated aqueous solution, apparently at a temperature lower than the crystallizing point of α, and higher than that of ε. It belongs to the right prismatic system; rectangular prisms terminated by four-sided summits, the faces of which are inclined to the lateral faces at angles of 115° and 125°. Sp. gr. = 151. Fuses in the fire less completely than ε. (Thomson, *Ann. Phil.* 26, 443.)

| | Calculation. | | Thomson. |
|---|---|---|---|
| NaO | 31·2 | 24·92 | 25·797 |
| $CO^2$ | 22·0 | 17·57 | 17·163 |
| 8HO | 72·0 | 57·51 | 56·920 |
| $NaO, CO^2 + 8Aq.$ | 125·2 | 100·00 | 99·880 |

ε. *With* 10 *Atoms of Water.*—The ordinary form of the salt as it crystallizes from a moderately concentrated solution at a comparatively low temperature. Crystalline system, the oblique prismatic (*Fig.* 114); frequently also with the *i*-surface; easily cleft parallel to *i*; $u : u^1 = 76° 12'$; $i : u$ or $u^1 = 108° 48'$; $i : a$ or $a^1 = 129° 52'$; $i : t = 121° 20'$; $u$ or $u^1 : t = 128° 6'$; $u^1 : m = 141° 54'$; $a : a^1 = 79° 44^1$ $a^1 : m = 140° 8'$; often hemitropic. (Brooke, *Ann. Phil.* 22, 287; *vid.* also Haidinger, *Pogg.* 5, 369.)—Sp. gr. = 1·423. (Haidinger.) When gently heated it fuses—the salt α crystallizing out, and leaving a liquid which contains more than 10 atoms of water and solidifies again at 33·5°. It effloresces quickly in the air, and passes at 38° into the salt α, and at 12·5° into the salt β. (Schindler.) In vacuo over oil of vitriol, at ordinary temperatures, it loses 9 atoms of water and is converted into the salt α; but if subsequently exposed to the air (saturated with moisture probably) for 10 days, it re-absorbs $8\frac{1}{2}$ atoms. (Von Blücher.) 143·2 parts (one At.) of the salt ε, exposed from 21st of Oct. to the 4th of Dec., to an atmosphere, the temperature of which ranged between 6° and 12°, and the dew-point from 2·8° to 3·9° below that temperature, lost on the first day only 3·2 parts of water—probably merely hygroscopic—and none at all afterwards. On the contrary, 53·2 parts (one atom) of fused carbonate of soda absorbs under similar circumstances, if pounded up from time to time, 88·2 parts (that is to say, nearly the whole 10 atoms) of water. On the other hand, carbonate of soda effloresces at 14·4°, if the dew-point stands at 8·9°. (H. Wattson, *Phil. Mag. J.* 12, 130.)

| | Calculation. | | Bergman. | Berthollet. | Darcet. |
|---|---|---|---|---|---|
| NaO | 31·2 | 21·79 | 20 | 20·25 | 20·35 |
| $CO^2$ | 22·0 | 15·36 | 16 | 12·15 | 16·04 |
| 10HO | 90·0 | 62·85 | 64 | 68·60 | 63·61 |
| $NaO, CO^2 + 10Aq.$ | 143·2 | 100·00 | 100 | 101·00 | 100·00 |

| | Thomson. | Kirwan. | Klaproth. | Bérard. | V. Rose. |
|---|---|---|---|---|---|
| NaO | 20·60 | 21·58 | 22 | 23·33 | 24 |
| $CO^2$ | 14·16 | 14·42 | 16 | 13·98 | 15 |
| 10HO | 65·24 | 64·00 | 62 | 62·69 | 61 |
| | 100·00 | 100·00 | 100 | 100·00 | 100 |

ζ. *Solution of Monocarbonate of Soda.*—One part of salt δ, dissolves in 1·56 parts of water at 17° (62·6° F.) (Thompson); 1 part of salt ε,

dissolves in 2 parts of cold, and in much less than 1 part of hot water. The solution saturated at 8° (46·4° F.) has a specific gravity of 1·107. (Anthon.)

*Amount of Anhydrous Carbonate of Soda in a given solution at* 15° (59°F.) *according to Tünnermann.* (*N. Tr.* 18, 2, 23.)

| Sp. gr. | Per cent. | Sp. gr. | Per cent. | Sp. gr. | Per cent. | Sp. gr. | Per cent. |
|---|---|---|---|---|---|---|---|
| 1·1816 | 14·880 | 1·1308 | 11·160 | 1·0847 | 7·440 | 1·0410 | 3·720 |
| 1·1748 | 14·508 | 1·1261 | 10·788 | 1·0802 | 6·768 | 1·0368 | 3·348 |
| 1·1698 | 14·136 | 1·1214 | 10·416 | 1·0757 | 6·396 | 1·0327 | 2·976 |
| 1·1648 | 13·764 | 1·1167 | 10·044 | 1·0713 | 6·324 | 1·0286 | 2·504 |
| 1·1598 | 13·392 | 1·1120 | 9·672 | 1·0669 | 5·972 | 1·0245 | 2·232 |
| 1·1549 | 13·020 | 1·1074 | 9·300 | 1·0625 | 5·580 | 1·0204 | 1·850 |
| 1·1500 | 12·648 | 1·1028 | 8·928 | 1·0578 | 5·208 | 1·0163 | 1·488 |
| 1·1452 | 12·276 | 1·0982 | 8·556 | 1·0537 | 4·836 | 1·0121 | 1·116 |
| 1·1404 | 11·904 | 1·0937 | 8·184 | 1·0494 | 4·464 | 1·0081 | 0·744 |
| 1·1356 | 11·532 | 1·0892 | 7·812 | 1·0452 | 4·092 | 1·0040 | 0·372 |

*b.* SESQUICARBONATE OF SODA.—Found native at Fessau as *Trona*, and in Mexico as *Urao*. (Rivero & Boussingault, *Ann. Chim. Phys.* 29, 110.) It crystallizes from an aqueous solution of the bicarbonate as the liquid cools after being concentrated by boiling (Phillips, H. Rose), or when the solution is evaporated in vacuo, over oil of vitriol. (Döbereiner, *Gilb.* 72, 215.) From a hot solution containing both carbonate and bicarbonate of soda, the two salts crystallize out by themselves on cooling; but if an aqueous solution of bicarbonate be rapidly boiled, so that it may lose only a part of its second atom of carbonic acid—or if the crystallized salt be heated to a temperature not exceeding 200°—or again, if equivalent proportions of carbonate and bicarbonate of soda are melted together and dried,—a mass is obtained, which, if exposed to the air in a cellar for some weeks, absorbs water, becomes perfectly crystalline, and contains spaces filled with shining crystals of sesquicarbonate of soda. (R. Hermann, *J. pr. Chem.* 26, 312.) If 4 oz. of alcohol be poured on the top of a solution containing 100 grains of simple carbonate and 152 grains of crystallized bicarbonate of soda in 4 ounces of water, fine clear acicular crystals are formed after several days at the surface of separation of the two liquids: these crystals consist of sesquicarbonate of soda, have an alkaline reaction, and do not effloresce in the air at 22·5. At the bottom of the solution, large crystals of the simple carbonate are formed, together with a crust of bicarbonate of soda. (Winckler, *Repert.* 48, 215.)

The crystalline system of Trona is the oblique prismatic (*Fig.* 93); $u : u^1 = 47° 30'$; $i : f$ (backwards) $= 103° 15'$; $i : u = 103° 45'$; easily cleavable parallel to $i$; less easily, parallel to $u$ and $f$; colourless, transparent, or pellucid; sp. gr. = 2·112. (Haidinger, *Pogg.* 5, 367.) Urao, is translucent, of foliated radiating structure and conchoidal fracture; alkaline and not efflorescent. (Rivero.) The ordinary crystals artificially prepared are small, of the same form as Trona, and permanent in the air. (H. Rose.) The salt when heated to redness, or when its aqueous solution is boiled for many hours (H. Rose), loses half its carbonic acid. It dissolves in water more readily than the bicarbonate, but less easily than the simple salt. The solution evaporated in vacuo over oil of vitriol, yields a mass of crystals composed of the simple carbonate and the bicarbonate together. (H. Rose, *Pogg.* 34, 160.)

The solution is not rendered turbid by 1 part of sulphate of magnesia dissolved in 10 parts of water. (Schindler.)

| | Crystallized. | | | Klaproth. *Trona.* | Boussingault. *Urao.* | Phillips. *Artificial.* |
|---|---|---|---|---|---|---|
| $2NaO$ | 62·4 | 40·15 | | 37·0 | 41·22 | 78·2 |
| $3CO^2$ | 66·0 | 42·47 | | 38·0 | 39·00 | |
| $3HO$ | 27·0 | 17·38 | | 22·5 | 18·80 | 21·8 |
| Sulphate of Soda | ,, | ,, | | 2·5 | ,, | ,, |
| Impurities | ,, | ,, | | ,, | 0·98 | ,, |
| $2NaO,3CO^2 + 3Aq.$ | 155·4 | 100·00 | | 100·0 | 100·00 | 100·0 |

| | Winckler. *Artificial.* | Hermann. *Artificial.* |
|---|---|---|
| NaO | 41·13 | 40·00 |
| $CO^2$ | 43·31 | 43·06 |
| HO | 15·56 | 16·94 |
| | 100·00 | 100·00 |

*c. Bicarbonate of Soda.* Found in alkaline mineral waters, and sparingly in several springs.

*Preparation.* The same as for bicarbonate of potash, according to methods 1, 2, 3, and 4.

1. A solution is employed containing 1 part of simple carbonate of soda in 2 parts of water.

2. Carbonate of soda which has effloresced in warm air (at 37°, *Schindler*) to a loose powder (containing at least 1 atom of water) is exposed to a current of carbonic acid gas. Absorption follows with great rapidity and great rise of temperature, sufficient even to fuse the mass. (Kreuzburg, *Kastn. Arch.* 16, 223; 17, 253.) The effloresced salt may be placed in sieves covered with paper, over the openings by which the carbonic acid escapes from the fermenting-tubs in the preparation of brandy: the salt is broken up daily, and becomes saturated in 8 days. (Mühlenbrook, *Repert.* 64, 42.) Berzelius (*Pogg.* 16, 434) spreads an intimate mixture of 1 part of 10-hydrated and 3 parts of anhydrous carbonate of soda, on linen stretched over iron rings; these he places one above another in a cylinder of tinned iron, through the lower opening of which the carbonic acid enters, whilst a bladder, from which the air has been expelled by pressure, is tied over the top. On the salt thus obtained, cold water is poured, and the whole stirred about; by this means, any simple carbonate which may still be mixed with it, is dissolved; after 12 hours, the salt left undissolved is drained and dried. Mohr (*Ann. Pharm.* 19, 15; 29, 268) introduces an intimate mixture of equal parts of 10-hydrated and anhydrous carbonate of soda into a long, wide tube of glass, and passes carbonic acid gas through the mixture. The mass becomes heated, commencing at the end at which the gas flows in; and the heat gradually increases till it reaches the other end; hence it is necessary to cool the tube. The saturation is complete in two hours, and the salt requires no purification. Or, he puts the mixture into a vessel of equal width at top and bottom—so that the mass, when it becomes dry and caked, can be easily withdrawn—closes it air-tight after the air has been expelled by a rapid current of carbonic acid gas, and passes the gas into it without intermission from his gas-generating vessel. The gas is at first somewhat slowly absorbed; but as the mass becomes heated, the absorption goes on

with great rapidity.—The crystals of the 10-hydrated salt may also be exposed to the action of carbonic acid; they then become covered with a white crust, and suffer the excess of water of crystallization to run off. (Schäffer, *Br. Arch.* 25, 251.) In this manner, a spongy, friable mass is obtained, which still retains its original form, but must be pulverized and repeatedly washed with cold water, to free it from simple carbonate still adhering to it, and then dried at a moderate heat. (R. Smith, P. Boullay, *J. Pharm.* 16, 118 and 123.) The salt must be rapidly dried after washing, because it loses carbonic acid if long exposed to the air in a moist condition; or it may be dried at 37°, and once more exposed to carbonic acid. (Schindler.)

3. From 3 to 4 parts of 10-hydrated carbonate of soda, are intimately mixed with 1 part of commercial carbonate of ammonia; the semi-fluid mass thus obtained, which evolves ammonia, is allowed to stand 24 hours, and then exposed to the sun on bibulous paper or on clean bricks. The last trace of ammonia escapes with the water, and bicarbonate of soda remains as a chalky mass. (Schäffer.) As the ammonia evolved in this process is lost, and it is difficult to evolve it in close vessels on account of the large proportion of water present (at 75° the carbonate of ammonia passes off undecomposed, *Schindler*), Schoy (*N. Br. Arch.* 2, 137) carefully mixes 50 parts of dry carbonate of soda in fine powder with 15 parts of the 10-hydrated carbonate and 41 parts of carbonate of ammonia, and heats the mixture in a distilling vessel immersed in a water-bath. The first $\frac{9}{12}$ of the ammonia are readily evolved, the following $\frac{2}{12}$ with greater difficulty, and the last $\frac{1}{12}$ is expelled by exposing the mass to the air. According to Schindler, a mixture of 3 parts of monohydrated carbonate of soda and 2 parts of carbonate of ammonia, exposed to the air at a temperature between 25° and 30°, yields pure bicarbonate; but at 75°, it evolves carbonate of ammonia and leaves simple carbonate of soda. The salt, however, is not obtained perfectly white, on account of organic substances contained in the carbonate of ammonia. Hoff (*Repert.* 25, 396) heats a saturated solution of 4 parts of 10-hydrated carbonate of soda, to which 1 part of carbonate of ammonia has been added, in a basin, till all smell of ammonia has passed off, filters hot, and leaves the solution to crystallize. Eight parts of the 10-hydrated salt, dissolved in 16 parts of water, together with 3 parts of carbonate of ammonia, evaporated in a water-bath and cooled, yield 4 parts of crystallized bicarbonate. (Winckler, *Mag. Pharm.* 19, 15.) When a solution of carbonate of soda, mixed with even an excess of carbonate of ammonia, is evaporated in the air at temperatures between 25° and 30°, the latter salt escapes and leaves simple carbonate of soda behind; if the mixture is heated in a retort, simple carbonate of ammonia passes over first, and afterwards sesquicarbonate sublimes. (Schindler.)

4. Planiava (*Kastn. Arch.* 9, 332) introduces a solution of 286·4 parts (2 atoms) of 10-hydrated carbonate of soda dissolved in twice the quantity of water, into a bottle; closes the bottle tightly with a stopper through which passes a tube-funnel drawn out to a very fine point at the end, and dipping an inch deep into the solution; pours slowly through this tube, 49 parts (one At.) of oil of vitriol, without agitation; and after it has stood quietly several days, separates the liquid from the crystals that are formed: these he washes with cold water and dries between bibulous paper. The bottle may be two-thirds filled with the solution, and the tube-funnel may pass to the bottom. When the solution prepared at a higher temperature has fallen to 50°, the oil of vitriol may be poured into the tube.

The finer the point, and the more slowly the oil of vitriol runs into the solution, the more beautiful are the crystals. The least shaking is disadvantageous, as carbonic acid is thereby evolved. (Schindler.) The salt may also be obtained by using acetic acid: in this case, agitation is necessary. (Schindler, *Mag. Pharm.* 33, 26.)

The salt is fully saturated with carbonic acid when it no longer reddens turmeric, or gives a precipitate with a very dilute solution of corrosive sublimate, but a white precipitate with a concentrated solution, becoming red in a few minutes, and then purple; with the least admixture of simple carbonate or sesquicarbonate of soda, the precipitate is reddish brown; but a salt not saturated precipitates corrosive sublimate white, if prepared by the third process and not quite free from carbonate of ammonia. (Schindler.)

Bicarbonate of soda is known only in combination with water; it crystallizes in oblique four-sided tables, which have a slight alkaline taste, no action on turmeric or litmus, turn logwood and reddened litmus blue, and syrup of violets green. (V. Rose.)

| | Calculation. | | Stromeyer. | R. Smith. | Berzel. | Schindler. |
|---|---|---|---|---|---|---|
| NaO | 31·2 | 37·05 | 37·06 | 37·82 | 89·26 | 89·31 |
| $2CO^2$ | 44·0 | 52·26 | 52·20 | 52·00 | | |
| HO | 9·0 | 10·69 | 10·74 | 10·18 | 10·74 | 10·69 |
| $NaO, 2CO^2 + Aq.$ | 84·2 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

| | V. Rose. | Berthollet. | Bérard. |
|---|---|---|---|
| NaO | 37 | 31·75 | 29·85 |
| $CO^2$ | 49 | 44·40 | 49·95 |
| HO | 14 | 23·85 | 20·20 |
| | 100 | 100·00 | 100·00 |

At a red heat, the crystals lose their water and one-half of their carbonic acid. The loss amounts to 36·8 per cent. (H. Rose.) They remain unaltered in dry air, but in moist air they gradually become turbid, then opaque and alkaline. In the state of powder, the salt is decomposed more rapidly; and if exposed to the air for a year, is converted into sesquicarbonate. When covered with a little water, it gives up carbonic acid in the air, even under 0°, but more rapidly in proportion as the temperature is higher, till it becomes changed into the simple carbonate, and as such is dissolved by the water. But a solution of the salt in 14 parts of water remains unchanged when exposed to the air. (Schindler.) An aqueous solution placed in a vacuum over oil of vitriol evolves carbonic acid without intermission, though with less rapidity than a solution of bicarbonate of potash, and loses 13·94 per cent., or about $\frac{1}{4}$ of the whole quantity of carbonic acid contained in it. If the solution is evaporated in a jar containing air, over oil of vitriol and hydrate of potash, and the residue dissolved in water and again evaporated, carbonate of soda is left behind nearly in a state of purity. By the continued boiling of an aqueous solution of the salt, 20·46 parts of the 52·2 per cent. of carbonic acid are evolved; and if the ebullition be further prolonged, nothing but simple carbonate remains. (H. Rose, *Pogg.* 34, 158.) A solution heated for a long while to 75°, loses barely $\frac{1}{4}$ of its carbonic acid. (R. Phillips.) This salt dissolves, according to V. Rose (*Scher. An.* 6, 52), in 13 parts of cold water; according to Berthollet (*N. Gehl.* 3, 52), *in 8 parts.*

## Sodium and Boron.

Borate of Soda.—a. Two-thirds Borate.—One atom of borax heated to redness with excess of carbonate of soda expels 2 atoms of carbonic acid. (Arfvedson.)

b. Monoborate.—On boiling a mixed aqueous solution of borax and carbonate of soda, carbonic acid is evolved. A mixture of 190·8 parts (one At.) of crystallized borax, and 53·2 parts (one At.) of dry carbonate of soda is heated to the melting point of silver. At first, the mass swells up considerably; when this has ceased, it is to be pressed together and again strongly heated; but even then it does not melt. The mass when cold, tastes caustic and alkaline, and dissolves easily in water with disengagement of heat.

*Combinations with Water.*

α. *With 6 Atoms of Water.*—When the 8-hydrated salt fused in its own water of crystallization is cooled to 0°, the salt α solidifies in confused crystals, with separation of a small quantity of mother-liquor.

β. *With 8 Atoms of Water.*—A solution of the dry salt in hot water (if too small a quantity of water is used, the crystallization is rendered more difficult), yields on slowly cooling in a covered vessel, large, oblique rhombic prisms. Angles of the lateral edges, about 130° and 170°; those contained between the oblique terminal face and the lateral edges are of about the same magnitude. The crystals melt at 57° in their own water of crystallization; and from the fused mass slowly cooled to 0°, crystals of the salt α separate. When the salt β is exposed to a higher temperature, it boils, and then solidifies, swelling up more strongly than borax, to a very friable, frothy mass, which rapidly absorbs carbonic acid from the air. The crystals also become turbid in the air, and are gradually converted into a mixture of borax and carbonate of soda. The same change takes place in the solution: but on boiling the latter, the carbonic acid is again gradually expelled. (Berzelius, *Pogg.* 34, 566.)

| | Calculation. | | | | Calculation. | | Berzelius. |
|---|---|---|---|---|---|---|---|
| NaO | 31·2 | 47·27 | | $NaO, BO^3$ | 66 | 55 | 55·15 |
| $BO^3$ | 34·8 | 52·73 | | 6HO | 54 | 45 | 44·85 |
| $NaO, BO^3$ | 66·0 | 100·00 | | α | 120 | 100 | 100·00 |

| | Calculation. | | Berzelius. |
|---|---|---|---|
| $NaO, BO^3$ | 66 | 47·83 | 47·99 |
| 8HO | 72 | 52·17 | 52·01 |
| β | 138 | 100·00 | 100·00 |

c. Biborate.—*Borax, Borax Veneta, Plinius' Chrysocolla.*—Found in combination with 10 eq. of water, as *Tinkal* or *Crude Borax*, in Asia. In Europe, this substance is purified from the earthy impurities and the greater part of the fatty or saponaceous matter adhering to it, by solution in water, filtration, and slow crystallization. Borax is now also prepared by mixing the boracic acid obtained from Tuscany with carbonate of soda, in the proportion of 10 parts of acid to 12 parts of the crystallized carbonate dissolved in hot water. Ordinary commercial borax may be *purified by* repeated crystallization; by fusion it is

obtained in the anhydrous state, as a clear brittle glass (*Glass of Borax*) which melts at a red heat. Vitrefied borax in the fused state dissolves many metallic oxides, and is therefore useful in experiments with the blow-pipe, in soldering, in the manufacture of glass, and as a flux in smelting operations. Borax has an astringent and somewhat alkaline taste, and a weak alkaline reaction on vegetable colours. Vitrefied borax becomes opaque in the air by absorbing a small quantity of water. Mixed with charcoal-powder, and exposed to the oxy-hydrogen blowpipe, it boils, gives off a white smoke, and is converted into a black substance which becomes white in the air. (Clarke.)

| | Calculation. | | Berzelius. | Arfvedson. | | Soubeiran. |
|---|---|---|---|---|---|---|
| | | | | Exp. 1. | Exp. 2. | |
| NaO | 31·2 | 30·95 | 30·827 | 30·8 | 31·4 | 31·416 |
| $2BO^3$ | 69·6 | 69·05 | 69·173 | 69·2 | 68·6 | 68·584 |
| $NaO,2BO^3$ | 100·8 | 100·00 | 100·000 | 100·0 | 100·0 | 100·000 |

*With Water it forms: α. Biborate of Soda with 5 Atoms of Water.—Octohedral Borax.* First obtained by Buron, and afterwards by Payen.—Borax is dissolved in water at 100°, till the solution has a specific gravity of 1·246, or 30° Bm. and then allowed to cool slowly. At 79°, the octohedrons begin to form, and continue to crystallize out till the temperature falls to 56°, when ordinary borax begins to appear. (Payen.) A solution of specific gravity 1·17 yields, on cooling, nothing but ordinary borax. (Payen.) If the solution be boiled for some hours, it appears to yield more octohedral borax on cooling, even when cooled below 56°. (Buron, Soubeiran & Pellerin, *J. Pharm.* 14, 170.) Forms regular octohedrons, of specific gravity 1·815; harder than ordinary borax, with a brilliant conchoidal fracture; not splitting in pieces from change of temperature. They become opaque in moist air from absorption of water.

| | Calculation. | | Payen. |
|---|---|---|---|
| $NaO,2BO^3$ | 100·8 | 69·14 | 69·36 |
| 5HO | 45·0 | 30·86 | 30·64 |
| Octohedral Borax | 145·8 | 100·00 | 100·00 |

*β. With 10 Atoms of Water.—Ordinary Borax.* Crystallizes from a less saturated solution below 56°. Vitrefied borax appears to be completely converted into the 10-hydrated salt by exposure to the air for several months in the state of powder. (Blücher.) Large, transparent, oblique, rectangular prisms belonging to the oblique prismatic system. (*Fig.* 103, 104), 105; $i : t = 106° 7'$; $i : m = 90°$; $u^1 : u = 91° 50'$; $u : t = 134° 5'$; $u : m = 135° 55'$. (Hauy.) Sp. gr. = 1·74 (Kirwan, Payen), = 1·757. (Wattson.) It flies to pieces when suddenly heated. Exposed to the air it effloresces on the surface only, and becomes opaque. When heated it loses water and swells up to a spongy mass (*Calcined Borax, borax usta*), which runs together at a red heat into glass of borax. Dissolves in 12 parts of cold and 2 parts of boiling water.

| | Calculation. | | Berzelius. | Kirwan. | Bergman. |
|---|---|---|---|---|---|
| NaO | 31·2 | 16·35 | 16·31 | 17 | 17 |
| $2BO^3$ | 69·6 | 36·48 | 36·59 | 34 | 39 |
| 10HO | 90·0 | 47·17 | 47·10 | 49 | 44 |
| *Ordinary Borax* | 190·8 | 100·00 | 100·00 | 100 | 100 |

| | L. Gmelin. | Thomson. | Payen. |
|---|---|---|---|
| NaO | 17·8 | 39·3 } | 53·05 |
| $2BO^3$ | 35·6 | 13·5 } | |
| 10HO | 46·6 | 47·2 | 46·95 |
| | 100·0 | 100·0 | 100·00 |

¶. d. Quadroborate.—A solution of ordinary borax is boiled with sal-ammoniac, in the proportion of 2 equivalents of borax to one of sal-ammoniac; ammonia is evolved if the solution is kept moderately dilute. As soon as the gas ceases to escape, the liquid is filtered and very slowly evaporated, when two crystalline crusts separate, one falling to the bottom, the other floating on the surface, although they possess the same appearance and chemical properties. They are either milk-white or transparent, and have a vitreous lustre. When heated they lose water and swell up, but not so strongly as borax. They dissolve in 5 or 6 parts of water at ordinary temperatures. A solution of this kind gives a granular precipitate of boracic acid, even with dilute acids. It precipitates solutions of all the salts which are thrown down by borax, but the precipitates frequently differ in colour and solubility from those obtained with borax. Like the latter, however, they lose boracic acid when washed with water. The solution is neutral to test paper.

| | Calculation. | | Bolley. |
|---|---|---|---|
| NaO | 31·2 | 11·92 | 11·50 |
| $4BO^3$ | 139·2 | 53·46 | 53·88 |
| 10HO | 90·0 | 34·61 | 34·61 |
| | 260·4 | 99·99 | 99·99 |

(P. Bolley, *Ann. Pharm.* 68, 122, 1848.) ¶.

e. Sexborate.—The aqueous solution of borax mixed with boracic acid till it no longer reddens turmeric, yields by evaporation and cooling, tabular crystals, which have a cooling taste, like nitre, and are neutral to vegetable colours. When heated, they swell up, evolving a small quantity of boracic acid, and afterwards melt to a clear glass. These crystals contain, according to Tünnermann, (*Kastn. Arch.* 20, 8), 30 per cent. of water. If 2 atoms of sulphuric acid are added to an aqueous solution of 3 atoms of borax, the mixture does not redden litmus, (because sexborate of soda is formed);

$$3(NaO, 2BO^3) + 2SO^3 = NaO, 6BO^3 + 2(NaO, SO^3);$$

but, on the addition of one atom more of sulphuric acid, the liquid slightly reddens the litmus, because the boracic acid is completely liberated; and if one drop more be added, the litmus acquires a bright red colour from the excess of sulphuric acid. (Laurent, *Ann. Chim. Phys.* 67, 218; *vid.* I., 152.)

## Sodium and Phosphorus.

A. Phosphide of Sodium.—Behaves, according to Gay-Lussac & Thénard, like phosphide of potassium. Lead-coloured; burns when heated in the air, and is converted into phosphate of soda. (H. Davy.) According to *Gay-Lussac & Thénard*, the compound obtained by heating

sodium to redness in contact with glacial phosphoric acid, has the same properties as that which is formed when potassium is used.

B. Hypophosphite of Soda.—Hypophosphite of lime is decomposed by carbonate of soda, and the alcoholic solution left to evaporate in vacuo. Crystallizes in tables which appear to be rectangular, and have a pearly lustre. At a red heat it evolves spontaneously inflammable phosphuretted hydrogen gas. Very deliquescent, but somewhat less so than the potash-salt. (H. Rose.) It also dissolves very readily in absolute alcohol. (Dulong.)

C. Phosphite of Soda.—Rhombohedrons inclining to the cubical form; very soluble in water and alcohol. (Dulong.)—An aqueous solution of carbonate of soda neutralized by pure phosphorous acid and evaporated in vacuo to a syrupy consistence, yields crystals which evolve hydrogen gas on being heated. (H. Rose, *Pogg.* 9, 28.)—Fourcroy & Vauquelin obtained with Pelletier's phosphorous acid and soda, inclined four-sided prisms, square laminæ and feathery crystals, having a cool pleasant taste, and containing 23·7 per cent. of soda, 16·3 of phosphorous (?) acid, and 60 per cent. of water,—efflorescent, giving out a yellow flame in the fire, and dissolving in 2 parts of cold, and nearly the same quantity of hot water.

D. Ordinary Phosphate of Soda.—One atom of phosphoric acid mixed with solution of soda in excess, or fused with an excess of carbonate of soda, takes up 3 atoms of soda and forms the salt *a*; from a solution of carbonate or acetate of soda, it takes up but 2 atoms of soda, and with one atom of water forms the salt *b*; heated with common salt, it unites with only one atom of soda, and with 2 atoms of basic water forms the salt *c*. (Graham.)

*a*. Triphosphate.—Described by Thomson (*Ann. Phil.* 26, 381; also *Pogg.* 6, 80) as phosphocarbonate of soda. One atom of diphosphate (*b*.) heated to redness with an excess of carbonate of soda expels one atom of carbonic acid, and thus combines with one atom more of soda. (Mitscherlich.) This salt is also formed when dipyrophosphate of soda is heated to redness with caustic soda or carbonate of soda, or when the mixed solutions are simply evaporated to dryness; but by mere boiling with solution of soda, even for many hours, the pyrophosphate is not altered. (Graham.) When the crystallized salt is heated to redness, a mass is obtained which does not fuse by increase of temperature,—but if heated in glass vessels, corrodes them like caustic soda. (Graham.)

*Crystallized.*—To a concentrated solution of ordinary diphosphate of soda, at least half as much soda as it contains is added in solution, the liquid evaporated till a film appears, and left to cool. The salt crystallizes out, and the mother-liquor retains nothing but the excess of soda. The crystals freed from the liquid are rapidly dissolved in twice the quantity of hot water, the liquid filtered, and then left to crystallize. (Graham.) Thin six-sided prisms perpendicularly truncated, with two more obtuse and two less obtuse summits. Permanent in dry air. (Graham.) Taste, cooling and alkaline. (Thomson.) They melt at 76·7°. Heated to redness in a platinum retort (to keep off carbonic acid), they lose 55·19 per cent. of water, but still retain nearly one per cent., which may be nearly all expelled, if the mass be powdered and again heated to redness; *completely and readily*, however, by heating to redness with oxide of

lead, or monophosphate of soda; the total loss of water then amounts to between 55·99 and 56·05 per cent. ¶. Gerhardt (*J. de Pharm.* 12, 57) finds that this last atom is reabsorbed, with disengagement of heat, when the anhydrous compound is treated with water; hence he assumes the formula of the salt to be $3NaO,HO,PO^5 + Aq$. ¶. The salt, when exposed to the air in the state of aqueous solution, absorbs carbonic acid, and is converted into diphosphate, and ultimately into carbonate; other equally feeble acids also withdraw the third atom of soda. It expels ammonia from nitrate of ammonia. With nitrate of silver it gives a yellow precipitate of triphosphate of silver, the supernatant liquid becoming neutral. One part of the crystals dissolves in 5·1 parts of water at 15·5°. (Graham.)

| | Anhydrous. | |
|---|---|---|
| $3NaO$ | 93·6 | 56·73 |
| $cPO^5$ | 71·4 | 43·27 |
| $3NaO,cPO^5$ | 165·0 | 100·00 |

| | Crystallized. | | Graham. |
|---|---|---|---|
| $3NaO$ | 93·6 | 24·57 | 24·70 |
| $cPO^5$ | 71·4 | 18·74 | 18·60 |
| $24HO$ | 216·0 | 56·69 | 56·03 |
| $3NaO,cPO^5 + 24Aq.$ | 381·0 | 100·00 | 99·33 |

*b.* DIPHOSPHATE.—*Phosphate of Soda* (simply), *Neutral Phosphate of Soda*, *Sal Mirabile Perlatum*, *Pearl Salt*.—Found in several animal fluids, especially in urine. It may be prepared by adding carbonate of soda to the aqueous phosphoric acid obtained from bone-ash (II., 129)—the liquid being kept at a boiling temperature, and the carbonate of soda added as long as effervescence continues; filtering to separate phosphate of lime and magnesia; boiling the liquid down, and leaving it to crystallize. To purify the salt completely from lime and magnesia, the solution mixed with carbonate of soda is evaporated to dryness, redissolved, filtered, and then left to crystallize as before. (Berzelius.) Any arsenious or arsenic acid possibly mixed with the phosphoric acid, is completely thrown down with the lime. (Anthon, *Repert.* 59, 338.)—This salt is known only in combination with water.

*α. With one Atom of Basic Water.*—The salt *β* or *γ* is heated to 300° (Clark), or placed in vacuo over oil of vitriol for some days. (Blücher.)—White mass, having a slightly saline but not unpleasant flavour, and changing the colour of violets to green. At a red heat it fuses, and is converted into dipyrophosphate of soda, with loss of 6·26 per cent. of water. (Clark, *Schw.* 57, 428.)

| | Calculation. | | Clark. |
|---|---|---|---|
| $2NaO$ | 62·4 | 43·7 | |
| $HO$ | 9·0 | 6·3 | 6·26 |
| $cPO^5$ | 71·4 | 50·0 | |
| $2NaO,HO,cPO^5$ | 142·8 | 100·0 | |

*β. With one Atom of Basic Water and* 14 *Atoms of Water of Crystallization.*—Formed by evaporating the aqueous solution at 33°, and leaving it to crystallize. The crystals have the same form as those of arseniate of soda with 15 atoms of water. They do not effloresce in the air; but at about 300° they lose 47·63 per cent. of water, and at a red heat, 3·47 per cent. more. (Clark, *Ed. J. of Sc.* 14, 311; also *Schw.* 57, 444.)

| | Calculation. | | Clark. |
|---|---|---|---|
| 2NaO | 62·4 | 23·21 | 48·90 |
| $cPO^5$ | 71·4 | 26·56 | |
| HO | 9·0 | 3·35 | 3·47 |
| 14HO | 126·0 | 46·88 | 47·63 |
| 2NaO, HO, $cPO^5$ + 14Aq. | 268·8 | 100·00 | 100·00 |

*γ. With one Atom of Basic Water and* 24 *Atoms of Water of Crystallization.*—The phosphate of soda of the Pharmacopeias.—An aqueous solution of the salt is evaporated and left to crystallize in the cold. Transparent oblique rhombic prisms. Crystalline system, the oblique prismatic. (*Fig.* 96, 97, 98, 99, 100, and others.) $i : t = 121° 30'$; $i : a = 148° 30'$; $i : a = 142° 9'$; $i : f$ (backwards) $= 129° 12'$; $i : h$ (backwards) $= 112° 5'$; $u : u^1 = 67° 50'$; $u : t = 123° 55'$; $u^1 : m = 146° 5'$; $u : h = 140° 58'$. (Mitscherlich.) $i : t = 121° 14'$; $i : f$ (backwards) $= 129° 12'$; $i : h$ (backwards) $= 112° 27'$; $u : u^1 = 67° 30'$; $u : t = 123° 45'$; $u^1 : m = 146° 15'$. (Brooke, *Ann. Phil.* 22, 286.)—The crystals effloresce rapidly in the air. According to Clark, they effloresce at a temperature between 11° and 17°, and are converted into the salt β. According to Gay-Lussac, they lose in very dry air 31·7 per cent. of water—that is to say—a little more than half the whole quantity. In vacuo over oil of vitriol they lose in 4 days 59·84 per cent. (24 At.); and if exposed in this state to the air during the month of August, they reabsorb 34·61 per cent. (14 At.) (*Blücher.*)—The crystals fuse at a gentle heat, and at about 300° lose 60·03 per cent. of water; at a red heat, they give up 2·49 per cent. more, and are converted into dipyrophosphate of soda. (Clark.) The salt when heated to fusion, continues fluid for a long time after cooling; then becomes syrupy, and at last solidifies to a radiated mass, having a silky lustre. (Marx.)

| | Ordinary phosphate of soda. | | Thénard. | Berzelius. | Clark. | Graham. | Malaguti. | Longchamp. |
|---|---|---|---|---|---|---|---|---|
| 2NaO | 62·4 | 17·39 | 17 | 17·67 | 37·48 | 37·1 | 16·71 | |
| $cPO^5$ | 71·4 | 19·90 | 15 | 20·33 | | | 18·80 | 18·78 |
| HO | 9·0 | 2·51 | 66 | 62·00 | 2·49 | 62·9 | 64 25 | |
| 24HO | 216·0 | 60·20 | | | 60·03 | | | |
| *b*, γ | 358·8 | 100·00 | 98 | 100·00 | 100·00 | 100·0 | 99·76 | |

This salt, according to Clark and Graham, is 2NaO, HO, $cPO^5$ + 24 Aq.; according to Malaguti (*Compt. rend.* 15, 229; also *J. pr. Chem.* 27, 51), it is 2NaO, HO, $cPO^5$ + 26 Aq. Clark comminuted his crystals, and freed them between bibulous paper from any adhering mother-liquor previously to analysing them. (*Vid.* Longchamp, *Compt. rend.* 15, 65; also *J. pr. Chem.* 27, 46.)

*δ. In solution.* The salt γ dissolves in 4 parts of cold and 2 parts of hot water. The solution has the power of absorbing a considerable quantity of carbonic acid gas, after which it effervesces with the stronger acids, and slightly reddens litmus paper, but much less so than carbonic acid water. (Pagenstecher, *Repert.* 72, 318.) The solution boiled for three weeks in glass vessels, attacks them a little, and on evaporation yields scales having a silky lustre and the composition of the salt γ; by recrystallization the ordinary crystals of this salt are obtained. (Graham, *Pogg.* 32, 54.)—The solution precipitates triphosphate of silver from the nitrate, setting free one-third of the nitric acid. (Clark.)

*c.* SIMPLE OR MONOPHOSPHATE.—Generally designated as *Acid Phosphate of Soda.*—1. Phosphoric acid is added to the solution of *b*, till the mixture no longer precipitates chloride of barium; it is then evaporated to a small bulk, and left to crystallize by itself for some days. (Mitscherlich.) If enough phosphoric acid be added to an aqueous solution of soda, to render the fluid neither acid nor alkaline, the diphosphate, which has an alkaline reaction, will crystallize out first, and the acid phosphate afterwards. If soda be mixed with phosphoric acid in excess, all the excess beyond one atom may be separated by alcohol, while the acid salt will remain in solution at the bottom, and after some time will assume a solid crystalline form. (Berzelius.) ¶. 2. When alcohol is added to a solution of ordinary phosphate of soda in nitric acid, acid phosphate of soda separates in the crystalline form, and nitrate of soda remains in solution. (A. Schwarzenberg.) ¶.

Crystallizes always in combination with the same quantity of water, in two forms, not reducible one to the other, on account of their peculiar angular relations, but both belonging to the right prismatic system. (1.) *Ordinary form.* The primary form is a right rhombic prism: (*Fig.* 61, 62, 63 and other forms.) $u^1 : u = 93° 54'$; $p : u = 90°$; $p : a = 125° 25\frac{1}{2}'$; $p : y = 134° 18'$; &c. &c.—(2.) *Second form, which is also that of the crystals of diarseniate of soda.* Primary form, an octohedron with rectangular base: *Fig.* 54 (never appearing by itself), 64 and others. $u : u^1 = 78° 30'$; $i : i = 126° 53'$; $i : ii = 161° 34'$; $a : u = 128° 18'$; $i : u = 106° 26'$, &c. (Mitscherlich.) By rapid evaporation, scaly crystals are obtained. It reddens litmus. Of the 4 atoms of water belonging to the crystals, 2 atoms which constitute the water of crystallization go off at 100°, and the 2 atoms of basic water are retained. Of the two latter, one atom escapes between 190° and 204° (374° and 399° 2′ F.) leaving monopyrophosphate of soda; and the last atom is almost entirely given up between 204° and 244° (399° 2′ and 471° 2′ F.), when metaphosphate of soda (*a*) remains; this is converted, just below a red heat, into the metaphosphate *b*, and at a red heat into the metaphosphate *c*. By heating the crystals rapidly to 204°, they become semi-fused and boil up, lose 3 atoms of water, and are converted into monopyrophosphate of soda. (Graham.) The salt dissolves very easily in water, but not in alcohol.—In solution it precipitates the nitrate of silver yellow, as a tri-acid salt; imperfectly, however, unless the nitric acid set free is neutralized with ammonia. (Graham.)

| | Dried at 100°. | | | Graham. |
|---|---|---|---|---|
| NaO | 31·2 | 25·87 | | |
| $cPO^5$ | 71·4 | 59·20 | | 84·7 |
| 2HO | 18·0 | 14·93 | | 15·3 |
| NaO, 2HO, $cPO^5$ | 120·6 | 100·00 | | 100·0 |

| | Crystallized. | | | Mitscherlich, Graham. |
|---|---|---|---|---|
| NaO | 31·2 | 22·51 | | |
| $cPO^5$ | 71·4 | 51·52 | | 73·76 |
| 4HO | 36·0 | 25·97 | | 26·24 |
| NaO, 2HO, $cPO^5$ + 2Aq. | 138·6 | 100·00 | | 100·00 |

E. PYROPHOSPHATE OF SODA.—*a. Dipyrophosphate.* Obtained in the anhydrous state by heating to redness the common diphosphate of soda, D, *b*. It fuses at a red heat to a transparent glass, which crystallizes on cooling to a white, opaque, angular mass. Dissolved in water, it exhibits an alkaline reaction. (Clark.) Heated to bright redness with twice its

weight of charcoal, it yields phosphorus. (Saussure.) (Does the silica of the retort contribute to this result?—*Gmelin.*) The dry salt dissolved in water, yields, on cooling, crystals containing 10 atoms of water. (Clark.) 100 parts exposed to the air, likewise absorb, in a few weeks, 66·8 parts (10 At.) of water, and no more; in vacuo over oil of vitriol, this water is again given up. (Von Blücher, *Pogg.* 50, 542.) The crystals belong to the oblique prismatic system (*Fig.* 89), $i : m = 111° 48'$ $i : a = 119° 36'$; $i : f$ backwards $= 118° 22'$; $i : s = 123° 33'$; $i : h = 103° 24'$; $m : f = 109° 50'$; $m : a = 121° 43'$; $m : h = 107° 30'$; $m : a$, over $a$, $= 101° 51$. (Haidinger.) At a temperature still under redness, the crystals lose all their water, except a trace. (Clark.)

This salt dissolves less easily in water than the ordinary diphosphate of soda. With nitrate of silver it gives a white precipitate without liberating nitric acid. (Clark, *Ed. J. of Sc.* 7, 298; also *Schw.* 57, 421.) The pyrophosphoric acid contained in a solution of this salt is not converted into ordinary phosphoric acid when boiled by itself, but rapidly when boiled with phosphoric, sulphuric, hydrochloric, nitric, or acetic acid. (Stronmeyer, *Schw.* 58, 132.) The salt boiled with water for three weeks in a glass flask, powerfully corrodes the glass, and, combining with its alkali, passes into the state of ordinary triphosphate of soda. (Graham.)

| | Anhydrous. | | |
|---|---|---|---|
| 2NaO | 62·4 | | 46·64 |
| $b$PO$^5$ | 71·4 | | 53·36 |
| 2NaO, $b$PO$^5$ | 133·8 | | 100·00 |

| | Crystallized. | | | Clark. |
|---|---|---|---|---|
| 2NaO | 62·4 | 27·89 | | |
| $b$PO$^5$ | 71·4 | 31·90 | | 59·28 |
| 10HO | 90·0 | 40·21 | | 40·72 |
| 2NaO, $b$PO$^5$ + 10Aq. | 223·8 | 100·00 | | 100·00 |

*b. Monopyrophosphate.*—1. Formed when the ordinary monophosphate or acid phosphate of soda, D, *c*, is exposed some hours to a heat between 190° and 204° (374° and 399° 2′ F.) whereby it loses 3 atoms of water and retains 1 atom, which is not driven off even at 235° (455° F.). (Graham.) —¶ 2. A. Schwarzenberg (*Ann. Pharm.* 65, 2) prepares this salt by dissolving the neutral compound, either crystallized or after fusion, in acetic acid (whereby cold is produced), and adding alcohol. The acid salt separates in a crystalline form, and is washed with alcohol, while acetate of soda remains dissolved in the alcoholic liquid. It forms a white crystalline powder, readily soluble in water; by allowing a solution of the neutral salt to mix slowly with a stratum of alcohol carefully poured upon it, the acid salt may be obtained in regular crystals. ¶ The effloresced mass dissolves easily in water. The solution has an acid reaction, and yields by evaporation a white friable crust, but no crystals. It precipitates chloride of barium, and when mixed with nitrate of silver, throws down white pulverulent pyrophosphate of silver, setting half of the nitric acid at liberty. Solution of soda converts it into dipyrophosphate of soda, E, *a*. (Graham.)

| | Calculation. | | | Graham. | Schwarzenberg. |
|---|---|---|---|---|---|
| NaO | 31·2 | 27·95 | | 91·98 | 27·50 |
| $b$PO$^5$ | 71·4 | 63·98 | | | 63·15 |
| HO | 9·0 | 8·07 | | 8·02 | 8·43 |
| *NaO, HO, $b$PO$^5$* | 111·6 | 100·00 | | 100·00 | 99·08 |

F. METAPHOSPHATE OF SODA.—According to the degree of heat used in its formation, this salt appears in three different forms, which though the same in composition ($NaO,aPO^5$), possess different properties, as if the pyrophosphoric acid passed by a gradual transition into metaphoric acid.

*a. Slightly heated.* If the simple pyrophosphate of soda, E,*b* (or the common acid phosphate) is kept for some days at a temperature between 205° and 244° (401° and 471·2° F.) it retains, of the 26·24° per cent. of water, only 2·73 per cent., and if heated to near 315° (599° F.) only 0·37 per cent. The residue is soluble in water, with the exception of about 7 to 18 per cent. of the salt *b*, which is formed at the same time. The filtered solution is neutral, and when evaporated dries up, without yielding any crystals, and forms a white crust, which contains 10·36 per cent. of water, after being dried at 100°. The solution precipitates chloride of barium; gives with nitrate of silver a white precipitate of pyrophosphate of silver, nitric acid being set free; and when treated with solution of soda, is converted into crystallizable dipyrophosphate. (Graham.)

*b. Strongly heated, insoluble.* Formed when the salt D,*c*, or E,*b*, or F, is heated for some minutes not quite to redness. If the heat is slowly applied, a dense heavy powder is obtained; but if rapidly, the salt fuses, and a hard semi-vitreous mass is produced. Both varieties behave alike; the powder scarcely dissolves in boiling water, even after a long time. Acids have no action on it, and solutions of the alkalis, after long digestion, extract only a portion of the phosphoric acid. (Graham.) According to Liebig, the phosphoric acid thus separated combines with the alkali in the form of tribasic phosphoric acid. ¶ Maddrell (*Mem. of Chem. Society of London*, 3, 273) prepares a similar modification of the metaphosphate by igniting nitrate of soda with phosphoric acid of a syrupy consistence, and removing the soluble portions with water. The residue is anhydrous, and nearly insoluble in water, but dissolves in acids whether concentrated or dilute. ¶

*c. Ignited.* Ordinary monophosphate of soda heated to redness enters into fusion without acting on glass, and yields, on cooling, a clear glass, which has a sweetish, not acid taste, reddens litmus, deliquesces in the air, and dissolves in water without producing heat. (Proust.) It dissolves very readily in water and alcohol. The acid reaction of the solution is so weak, that 4·3 parts of dry carbonate of soda added to a solution containing 100 parts of the fused salt, even produce an alkaline reaction. The solution evaporates at 38° in the air, becomes clammy, and ultimately dries up to a transparent gum. This, after being dried in vacuo over oil of vitriol, contains 11·14 parts (1·23 At.) of water in 102·6 parts (1 At.) of the salt. When it is exposed to a temperature of 204° for some days, only 8·44 parts (not quite 1 At.) of water remain, but it appears to be changed into monopyrophosphate of soda (E,*b*). A solution of this salt does not alter by long keeping, and not even by being boiled with soda; but when it is completely boiled down with soda, and the residue strongly heated in a sand-bath, ordinary triphosphate of soda is the result. (Graham, *Pogg.* 32, 56.)

¶ 2. Pyrophosphate of soda prepared from ordinary phosphate is mixed with an equal weight of sal-ammoniac, and rapidly heated to redness; ammonia is disengaged; and after the excess of sal-ammoniac has been expelled, the residue consists of a mixture of metaphosphate of soda and chloride of sodium. This mixture is boiled with alcohol diluted with an equal weight *of water*, which dissolves the common salt, and

leaves pure metaphosphate of soda. The salt thus obtained fuses to a beautiful transparent glass, which deliquesces in the air. A solution of pyrophosphate of soda, when boiled with sal-ammoniac, disengages ammonia. (Jamieson, *Ann. Pharm.* 59, 350, 1846.)—3. By exposing microcosmic salt to a regular and slowly increasing heat, dissolving the residue in water, and evaporating to the crystallizing point. The best crystals are obtained by exposing the liquid in a flat vessel to the air at a temperature of 30°. (II., 133.) The salt crystallizes in oblique rhombic prisms, $a : b = 120°$; $a : c = 73° 30'$; $b : e = 84° 30'$. The crystals contain 4 atoms of water. The salt dissolves in 4·5 parts of cold water; has a purely saline, cooling taste; and remains for a long time undecomposed in a cold aqueous solution. After boiling for some time, the liquid acquires an acid reaction. Insoluble in absolute alcohol; dissolves with very great difficulty even in dilute alcohol. (Fleitmann & Henneberg, *Ann. Pharm.* 65, 304.)

| | Calculation. | | Maddrell. | | Fleitmann & Henneberg. |
|---|---|---|---|---|---|
| NaO | 31·2 | 30·10 | 30·117 | | |
| $a PO^5$ | 71·4 | 69·90 | 69·883 | | 70·18 |
| NaO, $a PO^5$ | 102·6 | 100·00 | 100·000 | | |

Fleitmann & Henneberg have likewise prepared the compounds $6NaO, 4PO^5$ and $6NaO, {}^5PO^5$, by fusing together a mixture of $2(6NaO, 3PO^5) + (6NaO, 6PO^5)$ that is $2NaO, PO^5 + NaO, PO^5$; or a mixture of $(6NaO, 2PO^5) + (6NaO, 6PO^5)$—or, according to the ordinary view, $3NaO, PO^5 + 3(NaO, PO^5)$—which corresponds to 187·27 parts of metaphosphate of soda and 100 parts of tribasic phosphate (D, *a*). The second compound is obtained in a similar manner by fusing $2(6NaO, 6PO^5)$ with $(6NaO, 3PO^5)$ or 307·5 parts of metaphosphate of soda with 100 parts of pyrophosphate. (Vid. II. 134.) From the solutions of these new salts, the corresponding compounds of the earths may be prepared, and likewise the compound $(4NaO, 2HO, 4PO^5)$ by dissolving the anhydrous salt in acetic acid, and precipitating with alcohol. It must be observed, however, that the existence of these new salts is not satisfactorily established; and MM. Laurent & Gerhardt are inclined to regard them as nothing more than pyrophosphates of soda intermediate between the neutral and acid salts already known, inasmuch as in the analyses of Fleitmann & Henneberg the water was merely determined by loss, and the absence of soda in the precipitates was not proved. (Vid. *Comptes rend. des Travaux de Chim.* 1, 12, 1849.) ¶

## Sodium and Sulphur.

A. Monosulphide of Sodium.—Sodium and sulphur unite when heated together, giving rise to vivid inflammation (H. Davy, Gay-Lussac & Thénard); also at ordinary temperatures (Winkelblech).—1. By heating to redness a mixture of sulphate of soda and charcoal, a flesh-coloured mass is obtained, which volatilizes at a red heat, burns gradually if heated in the air, producing sulphate of soda, and dissolves in water with disengagement of heat. (Berthier.) According to Gay-Lussac, $\frac{1}{6 \cdot 7}$ of the soda remains undecomposed in this process, even at a strong red heat, so that the reduced sodium is combined with somewhat more than 1 atom of sulphur.—2. Dry sulphuretted hydrogen gas passed over

hydrate of soda in coarse powder is freely absorbed, with formation of a flesh-coloured mass, and production of a degree of heat above 100°, so that the water formed, and partly also that belonging to the hydrate, is carried off in steam. (Kircher, *Ann. Pharm.* 31, 339.) ¶ Hydrate of soda and sulphur, when fused together, yield monosulphide of sodium and hyposulphite of soda, as in the case of potash; but the temperature required for the soda-compound is 275°, a little above which it suffers decomposition. (Fordos & Gelis.) ¶ In a state of fusion, sulphide of sodium attacks glass and acquires a yellow colour. (Berzelius.)

By dissolving monosulphide of sodium in water, or by half-saturating a solution of soda with hydrosulphuric acid gas (III., 31), a colourless solution of monosulphide of sodium or *hydrosulphate of soda* is obtained, which, when evaporated and cooled out of contact of air, yields colourless crystals, the form of which is an elongated rectangular prism with four-sided summits (Vauquelin, Berzelius); octohedrons (Vauquelin, Kircher). L'Hermina (*J. Polytechn.* 11, 337) obtained oblique rhombic prisms (*Fig.* 85) without the $a$ and $f$ surfaces; $i$ : the edge between $u^1$ and $u = 104°$; $u^1 : u = 110$; $u^1 : t = 125°$. This compound tastes somewhat hepatic at first, then caustic, alkaline, very bitter; it reddens litmus. (Berzelius.) The crystals, when fused in a retort, give off water and are converted into dry monosulphide of sodium. They become moist in the air, without however deliquescing, and change into sulphate of soda. (Berzelius.) An aqueous solution exposed to the air yields equal proportions of hyposulphite and 6-hydrated carbonate of soda. (Mitscherlich, *Pogg.* 8, 441.) This salt is very soluble in water, but less so in alcohol, which partly precipitates it from a concentrated aqueous solution. (Berzelius, *Pogg.* 6, 437.)

| | Octohedrons. | | Kircher. | Or: | | |
|---|---|---|---|---|---|---|
| Na | 23·2 | 19·30 | 19·30 | NaO | 31·2 | 25·96 |
| S | 16·0 | 13·31 | 13·85 | HS | 17·0 | 14·14 |
| 9HO | 81·0 | 67·39 | 67·10 | 8HO | 72·0 | 59·90 |
| NaS, 9Aq. | 120·2 | 100·00 | 100·25 | NaO, HS + 8Aq. | 120·2 | 100·00 |

B. Sulphide of Hydrogen and Sodium.—When sodium is heated in sulphuretted hydrogen gas, it takes fire and absorbs all the sulphur of a quantity of the gas equal in volume to the hydrogen which the sodium would have evolved from water; besides this, it absorbs $\frac{1}{3}$ of the same volume of undecomposed hydrosulphuric acid. The compound evolves with hydrated acids $\frac{4}{3}$ as much sulphuretted hydrogen as the sodium made use of would have produced of hydrogen gas. (Gay-Lussac & Thénard.) The compound should therefore consist of 3 atoms of sodium, 4 of sulphur, and one of hydrogen; but it more probably contains one atom of sodium, 2 atoms of sulphur, and one atom of hydrogen.

When solution of soda is saturated with hydrosulphuric acid gas, a colourless liquid is obtained, which may be considered as solution of sulphide of hydrogen and sodium, or as bihydrosulphate of soda. It yields colourless, deliquescent crystals, soluble in alcohol. (Berzelius.) According to Guéranger (*J. Chim. Med.* 15, 49), it yields no crystals. By boiling, it loses one half of its sulphuretted hydrogen; and on cooling, hydrated monosulphide of sodium crystallizes out.

Sodium is also capable of uniting with more than one atom of sulphur, probably indeed, like potassium, with as many as five. By heating dry carbonate of soda with an equal quantity of sulphur, *soda-liver of sulphur* is obtained, which, according to the experiments of Vauquelin (Ann.

*Chim. Phys.* 6, 32), may be considered as a mixture of sulphate of soda with tetrasulphide of sodium. The mass treated with nearly absolute alcohol, dissolves, leaving the sulphate of soda behind, and yields sometimes a crop of opaque, yellow needles united in tufts, and sometimes yellow transparent cubes. The aqueous solution of the polysulphide of sodium is yellow, has the same properties as that of the polysulphide of potassium, and may be assumed to contain hydrosulphite of soda ($NaS^6 + HO = NaO, HS^5$.

C. Hyposulphite of Soda.—1. A boiling solution of soda is saturated with sulphur, and then added to a perfectly neutral solution of sulphite of soda, till the mixture acquires a decided yellow colour. The liquid is filtered, evaporated to a small bulk, and cooled, and the crystals obtained are purified from adhering sulphide of sodium by recrystallization. (A. Lenz, *Ann. Pharm.* 40, 94.)—2. Sulphurous acid gas is passed through a solution of soda which has been saturated with sulphur at a boiling heat, till a filtered portion appears of a faint yellow, but not altogether colourless,—because, if a small quantity of sulphide of sodium is left in the solution, that substance oxidizes first in the air, and so prevents the decomposing action of the atmosphere on the hyposulphite of soda. The filtrate is rapidly evaporated to a syrupy consistence—filtered again, if necessary—one measure of the liquid well shaken with half a measure of alcohol—and the whole set aside at rest. Below the yellow alcoholic stratum containing sulphide of sodium, the hyposulphite of soda crystallizes out from its solution in water, in large colourless crystals. (Capaun, *J. pr. Chem.* 21, 310.)—3. Two parts of anhydrous sulphate of soda are heated to redness with one part of charcoal; and the mass, which contains sulphide of sodium, left to cool, and then boiled with water and one part of sulphur; the filtrate, when sufficiently concentrated, is exposed to the air in a basin, and the crystals formed are purified from adhering sulphur by re-crystallization. This process takes a long time.—4. An aqueous solution of sulphite of soda is saturated with sulphur in a close vessel, then filtered, and evaporated to the crystallizing point. The liquid rapidly deposits sulphur and yields principally sulphate of soda. (Capaun.)—¶ 5. One pound of pure crystallized carbonate of soda is dried as perfectly as possible, and intimately mixed with 5 ounces of pure sulphur—the mixture gradually heated in a glass or porcelain basin to the melting point of the sulphur, and kept at that temperature for some time, stirring constantly, in order to bring every part in contact with the air. The sulphide of sodium formed at first, absorbs oxygen from the air, and is converted, with feeble incandescence, into hyposulphite of soda. The mass when cold is dissolved in water, boiled with sulphur for some time, and the filtrate evaporated to the crystallizing point. Very fine and pure crystals are obtained in this manner. If the heat employed is too strong, part of the sulphur is burned off and carbonate of soda remains undecomposed; in this case a second crystallization is necessary. (Walchner, *Ann. Pharm.* 46, 235.) ¶

Hyposulphite of soda crystallizes, according to Mitscherlich (*Pogg.* 12, 140), from a hot aqueous solution, uncombined with water of crystallization; from a less concentrated solution it crystallizes, as it cools, in large, clear, oblique prisms belonging to the right prismatic system, nearly resembling *Fig.* 87; but between the two *u*-faces there are two *z*-faces in addition; $i$ : the axis $= 76° 2'$; $i : a = 165° 5'$; $i : t = 90°$; $a : t = 104° 55'$; $u^1 : t = 124° 15'$; $u : z = 164° 30'$; $z : z = 142° 24'$. (Prevos-

taye, *N. Ann. Chim. Phys.* 3, 353; *Compt. rend.* 13, 873.) The *i*-surface stands obliquely on the acute lateral edges, which are truncated. (Rammelsberg.) Inodorous, tastes cooling, afterwards bitter, slightly alkaline and sulphurous. (Vauquelin, *Scher. Anno* 8, 170.) It has no alkaline reaction; remains unaltered in the air. (Chaussier, *Scher. J.* 8, 470.) The crystallized salt fuses when heated, and remains fluid a long time after cooling; if the heat be carefully applied, the salt loses, without decomposition, 35·97 per cent. of water (Rammelsberg); at a higher temperature sulphur is evolved, and a brownish mixture left, consisting of sulphide of sodium and sulphate of soda. (Vauquelin, Rammelsberg, *Pogg.* 56, 298.) Heated in the open air, it burns with a blue flame. (Chaussier.) It dissolves readily in water, but not in alcohol. In close vessels, the aqueous solution deposits sulphur till nothing but sulphite of soda remains in the liquid; exposed to the air, it deposits sulphur, and is converted into sulphate of soda. (Cassaun.)

| | Crystallized. | | Rammelsberg. |
|---|---|---|---|
| NaO | 31·2 | 25·12 | 24·96 |
| $S^2O^2$ | 48·0 | 38·65 | |
| 5HO | 45·0 | 36·23 | 35·97 |
| $NaO,S^2O^2 + 5Aq.$ | 124·2 | 100·00 | |

An aqueous solution of 2 atoms of hyposulphite of soda dissolves one atom of iodine without becoming coloured, and still remains neutral; it then contains one atom of iodide of sodium and one atom of a compound consisting of one atom of soda with a new acid of sulphur (*bisulphuretted hyposulphuric acid* (or tetrathionic acid), which contains 5 atoms of oxygen to 4 atoms of sulphur.

$$2(NaO,S^2O^2) + I = NaI + NaO,S^4O^5.$$

On boiling the solution, the salt is resolved into free sulphur, sulphurous acid which escapes, and sulphate of soda which remains dissolved. (Fordos and Gélis, *Compt. rend.* 15, 920.)

¶ D. Pentathionate of Soda. (*Vid.* Pentathionic acid.)—$NaO,S^5O^5$. An unstable compound known only in solution.

E. Tetrathionate of Soda.—$NaO,S^4O^5$. (*See above.*) Kessler (*Pogg.* 74, 249) prepares this salt by dropping a neutral solution of chloride of copper into a solution of hyposulphite of soda till a precipitate appears, and then mixing with alcohol. The salt fuses in its own water of crystallization, with separation of sulphur and evolution of sulphurous acid.

F. Trithionate of Soda.—$NaO,S^3O^5$. Prepared in the same manner as the corresponding potash-compound. ¶

G. Sulphite of Soda.—a. *Monosulphite.*—Obtained in the same manner as sulphite of potash. Known only in combination with water. Transparent, colourless, flattened, four and six-sided prisms, with dihedral summits; having a fresh taste, afterwards sulphurous, and turning reddened litmus-paper blue. It contains in 100 parts, according to Fourcroy and Vauquelin, 18·8 parts of soda, 31·2 parts of sulphurous acid, and 50 parts of water (= 8 atoms). Changes gradually in the air into sulphate of soda. Fuses *when heated, gives off* water and sulphur, and is converted

into sulphate of soda with excess of base. Dissolves in 4 parts of cold water, with reduction of temperature, and in less than an equal quantity of boiling water. (Fourcroy & Vauquelin, *Ann. Chim.* 24, 264; also *Crell. Ann.* 1800, 2, 405.) Muspratt obtained this salt combined with 10 equivalents of water, corresponding to the carbonate. It is most soluble in water at 33° (91·4° F.), and less soluble at higher temperatures. (Mitscherlich.)

b. *Bisulphite.*—An aqueous solution of carbonate of soda is saturated with sulphurous acid gas. Crystallizable; does not redden litmus. (Gay-Lussac & Welter.) ¶ Obtained in a similar manner by Muspratt, in opaque crystals. Precipitated in a granular form by alcohol from a solution of soda saturated with sulphurous acid. Less soluble in water than bicarbonate of soda; has an acid reaction and unpleasant sulphurous taste; evolves sulphurous acid in the air; decrepitates when heated, and is resolved into sulphate of soda and free sulphur.

| | Calculation. | | Muspratt. | | Calculation. | | Muspratt. |
|---|---|---|---|---|---|---|---|
| NaO | 31·2 | 20·41 | 20·46 | NaO | 31·2 | 29·96 | 29·04 |
| $SO^2$ | 32·0 | 20·90 | 20·47 | $2SO^2$ | 64·0 | 61·42 | 60·20 |
| 10HO | 90·0 | 58·69 | 59·07 | HO | 9·0 | 8·62 | 10·76 |
| *a* | 153·2 | 100·00 | 100·00 | *b* | 104·2 | 100·00 | 100·00 ¶ |

H. Hyposulphate of Soda.—An aqueous solution of hyposulphate of baryta is precipitated at a boiling heat by carbonate of soda, then filtered and evaporated. Large transparent prisms belonging to the right prismatic system (*Fig.* 77), but without the *t* and *n*-faces; $i : a = 152° 54'$; $i : t = 121° 6'$; $a : a = 125° 18'$; $a : u = 130° 9'$; $u : u = 90° 38'$; $u : m = 135° 12'$. The crystals have a bitter and peculiar taste, are permanent in the air, decrepitate slightly when heated, and on being heated to redness, leave 58·24 per cent. of sulphate of soda. They dissolve in 2·1 parts of water at 16°, and in 1·1 part at a boiling heat; the solution is not decomposed by boiling. Insoluble in alcohol. (Heeren, *Pogg.* 7, 76.)

Crystallized, according to Heeren.

| | | |
|---|---|---|
| NaO | 31·2 | 25·74 |
| $S^2O^5$ | 72·0 | 59·41 |
| 2HO | 18·0 | 14·85 |
| NaO, $S^2O^5$ + 2Aq. | 121·2 | 100·00 |

I. Sulphate of Soda.—*a.* Monosulphate.—*Glauber's Salts, Sal mirabile Glauberi.*—Found in the anhydrous state, effloresced on the surface of the ground by the heat of the sun, as *Thenardite;* in the state of solution in sea-water, in salt springs, and many other mineral waters.—1. Obtained from certain mineral waters by evaporation and subsequent cooling.—2. Many salt springs, and frequently also the mother-liquor obtained from common salt, yield crystals of Glauber's salt at freezing temperatures. This may either be present naturally, or it may be formed from common salt and sulphate of magnesia contained in the liquid,—these salts decomposing each other in the cold (at a temperature of + 10°, according to Balard, *J. Pharm. et Chim.* 6, 406) by double affinity (I., 131); the mother liquor obtained from sea-water behaves in this way. The solid residue of the salt-pans also, freed from common salt by cold water, frequently yields Glauber's salt when boiled.—3. By heating common *salt with sulphuric* acid, whereby hydrochloric acid is also obtained at the

same time.—4. From the residue obtained in the preparation of chlorine by common salt, sulphuric acid, and peroxide of manganese. Part of the residue is heated to redness with charcoal; the resulting sulphide of sodium dissolved out by water; and the manganese precipitated by it from the aqueous solution of the remaining portion.—5. A solution of common salt and of ferrous or ferric sulphate is exposed to a freezing temperature, at which temperature sulphate of soda crystallizes out; or the mixture is heated to redness, by which means the chloride of iron partly volatilizes, and the rest is resolved by the oxygen of the air into chlorine and sesquioxide.—6. A by-product in the preparation of sal-ammoniac (II., 478) and magnesia alba, and in the amalgamation of silver ore.—7. May be obtained from many glass slags (*Glasgalle*), if native or artificial soda has been used in the preparation of the glass.—8. By exhausting with water the ashes of *Tamarix gallica*.

The salt is obtained as an anhydrous mass, by leaving the 10-hydrated salt to effloresce or by heating it to redness; or according to Faraday (*N. Quart. J. of Sc.* 3, 223), in anhydrous crystals, by evaporating an aqueous solution at a temperature considerably below 100°; according to Mitscherlich, even at 40°. The anhydrous salt forms in crystals belonging to the right prismatic system; rhombic octohedrons (*Fig.* 59), partly still retaining the *i*-surface (from *t* to the vertex). $a : a^{II} = 135° 41'$; $a : a^{I} = 123° 43'$; $a^{I} : a^{II} = 104° 18'$; $u^{I} : u = 129° 21'$; $a^{I} : t = 134° 19'$; $u : t = 125° 19\frac{1}{2}'$; readily cleaving parallel to *t* and *a*. (Mitscherlich, *Pogg.* 12, 138; 25, 301.) The Thenardite of Aranjuez has the same form; $u^{I} : u$ nearly $= 125°$ (Casaseca & Cordier, *Ann. Chim. Phys.* 32, 308.) Thomson (*Ann. Phil.* 28, 401) obtained rhombic octohedrons in which $a : a^{I} = 75°$ and $a : a^{II} = 140°$. The crystals are transparent. The fused salt solidifies on cooling to a transparent, crystalline, foliated mass. The specific gravity of the crystals = 2·73 (Cordier), 2·645 (Thomson); that of the solid fused salt = 2·6313 (Karsten). The crystals, when exposed to the air, become opaque on the surface by absorbing water. At a strong red heat, the salt melts to a thin liquid. Its taste is bitter and saline, and in the hydrated state cooling at the same time. According to Morveau, it has an alkaline reaction on logwood, but not on turmeric. By ignition with charcoal, it is changed into monosulphide of sodium. Milk of lime converts it in solution, though but imperfectly, into gypsum and soda. (Scheele, *Opusc.* 2, 170; Gren, *Crell. Auswahl d. n. entdeck.* 8, 111.) With chloride of potassium or nitrate of potash it yields sulphate of potash. (Karsten.) Hydrochloric acid gas has no effect on the anhydrous salt; solution of hydrochloric acid converts it into chloride of sodium and bisulphate of soda. (Kane.)

| | Anhydrous. | | Berzelius. | Longchamp. | Kirwan. |
|---|---|---|---|---|---|
| NaO | 31·2 | 43·82 | 43·72 | 43·86 | 44 |
| $SO^3$ | 40·0 | 56·18 | 56·28 | 56·14 | 56 |
| NaO, $SO^3$ | 71·2 | 100·00 | 100·00 | 100·00 | 100 |

| | Wenzel. | Dalton. | Bérard. |
|---|---|---|---|
| NaO | 44·3 | 45·2 | 47·22 |
| $SO^3$ | 55·7 | 54·8 | 52·78 |
| | 100·0 | 100·0 | 100·00 |

*Combinations with Water:*

*α. With 8 Atoms of Water.*—Crystallizes from the fused 10-hydrated salt at a temperature of 12° (53·6° F.) (Ziz); also from a solution of this salt in half its weight of water at 7° (44·6° F.), and above that temperature, if the fluid remains undisturbed in a covered vessel. (Ziz, Faraday, *vid.* I., 10.) Double four-sided pyramids, or elongated four-sided tables, with acuminated edges (Ziz); four-sided prisms, with dihedral summits (Faraday); transparent; much harder than the 10-hydrated salt. (Faraday, *Quart. J. of Sc.* 19, 152; also *Pogg.* 6, 82.) As the 10-hydrated salt crystallizes out on agitation, contact of air, &c., from the remaining liquid, the crystals of the 8-hydrated salt become white and opaque: and even when the liquid above them is mixed with warm water, the whole poured off, and an attempt made to loosen the crystals with a rod, the opacity spreads from the point of contact, and radiates through the whole crystalline mass, which becomes heated and quite dry throughout, probably from formation of the 10-hydrated salt. (Ziz, *Schw.* 15, 166.)

| | 8-hydrated salt. | | Faraday. | | Ziz. |
|---|---|---|---|---|---|
| $NaO, SO^3$ | 71·2 | 49·72 | 50 | | 45 to 50 |
| 8HO | 72·0 | 50·28 | 50 | | 55 „ 50 |
| $NaO, SO^3 + 8Aq$ | 143·2 | 100·00 | 100 | | 100 „ 100 |

*β. With 10 Atoms of Water.*—The ordinary crystals of Glauber's salt are produced at a lower temperature, and from a more dilute solution than the above. Crystalline system, the oblique prismatic (*Fig.* 119); $i : t = 107° 44'$; $i : a = 113° 18'$; $i : u$ or $u^1 = 101° 20'$; $i : f$ backwards $= 130° 45'$; $u : u^1 = 80° 24'$; $u : t = 130° 12'$; $u : v = 162° 38'$; $u : m = 139° 48'$.) Brooke, *Ann. Phil.* 23, 21.) Also (Prevostaye, *Ann. Chim. Phys.* 78, 354.) The crystals are very large, transparent, and of specific gravity = 1·35. (Thomson.) They effloresce in the air, losing all their water. (Gay-Lussac.) They effloresce completely in an atmosphere at 14·5°, when the dew-point stands at 9·5°, but no longer when the dew-point is above 10° (H. Wattson), they also lose the whole of their water in vacuo over oil of vitriol, and re-absorb none from the air. (Von Blücher.) The perfectly effloresced salt swells in very moist air to three times its bulk, and then becomes a crystalline mass of ordinary Glauber's salt, with a slight excess of water. (Graham, *N. Quart. J. of Sc.* 6, 557.) In air completely saturated with moisture, the effloresced salt deliquesces perfectly in 80 days. (R. Brandes, *Schw.* 51, 430.) When the crystals are gently heated, the greater part fuse, withdrawing the water from that portion which separates in the anhydrous state, and forming a solution, which, according to Faraday, appears to contain, at 82·2°, 18 atoms of water to 1 atom of the dry salt. According to Brandes and Firnhaber, the fusion begins at 31°, and is as far as possible complete at 37·5°. The salt hereby separated in the solid form contains less water in proportion as the temperature is higher; that which separates at 37·5° contains 43; that between 50° and 62° contains 35; that at 75° contains 20·7, and that 100° contains 14·5 per cent. of water. Cold alcohol does not withdraw any water from the powdered crystals, but 2 parts of alcohol acting on 1 part of the crystals at 37·5° (99·5° F.) leave a salt which contains only 32·5 per cent. of water. (Brandes & Firnhaber.)

| | 10-hydrated salt. | | Bergman. | Kirwan. | Berzelius. |
|---|---|---|---|---|---|
| NaO | 31·2 | 19·35 | 15 | 18·48 | 19·24 |
| $SO^3$ | 40·0 | 24·82 | 27 | 23·52 | 24·76 |
| 10HO | 90·0 | 55·83 | 58 | 58·00 | 56·00 |
| NaO, $SO^3$ + 10Aq. | 161·2 | 100·00 | 100 | 100·00 | 100·00 |

| | Wenzel. | Bucholz. | Brandes & Firnhaber. |
|---|---|---|---|
| NaO | 19·5 | 20 | 19·1 |
| $SO^3$ | 24·3 | 23 | 24·4 |
| 10HO | 55·2 | 57 | 56·5 |
| | 99·0 | 100 | 100·0 |

γ. *Aqueous solution.*—One part of the 10-hydrated salt requires for solution 8·22 parts of water at 0°; 2·08 parts at 18°; 1 part at 25°; 0·37 parts at 32°; 0·31 parts (the smallest quantity) at 33°; and 0·38 parts at 50·4°. (Gay-Lussac.) At 33°, 15·5 atoms of water take up one atom of the anhydrous salt. One part of the crystals dissolves, at 7·5°, in 6·1; at 12·5°, in 3·44; at 18·75°, in 2·41; at 25°, in 0·7; at 31·25°, in 0·21; at 37·5°, in 0·34; at 43·75°, in 0·38; at 50°, in 0·39; at 56°, in 0·4; at 62·5°, in 0·45; at 69°, in 0·41; at 75°, in 04·2; at 81°, in 0·46; at 87°, in 0·45; at 94°, in 0·44; and at 100°, in 0·41 parts of water. (Brandes & Firnhaber, *Br. Arch.* 7, 151.) One part of the crystallized salt dissolves at 20° (68° F.) in 1·724 parts of water, forming a solution of specific gravity 1·1259. (Karsten.) A solution saturated at 33° deposits crystals of the anhydrous salt at 100°. (Faraday, Haidinger, Mitscherlich.) According to Brandes & Firnhaber, the salt which separates still contains 27·8 per cent. of water; and alcohol precipitates the 10-hydrated salt from a cold saturated solution. [Tables of specific gravity, per centage, and boiling point of the solution by Brandes & Gruner, *Br. Arch.* 22, 148.]

Thomson describes a *sesqui-sulphate* of soda, which exists in the residue left after the preparation of hydrochloric acid; crystallizes in rectangular prisms; and contains no water: it requires, however, more accurate examination. (*Ann. Phil.* 26, 436; also *Pogg.* 6, 80.)

*b.* Bisulphate.—Obtained in the anhydrous state by heating 10 parts of dry sulphate with 7 parts of oil of vitriol, till the mixture remains tranquil at a dull red heat. (Berzelius.) By dissolving this mass in twice its weight of hot water and then cooling, it is obtained in hydrated crystals (Berzelius); or by dissolving Glauber's salt in dilute sulphuric acid, evaporating, and cooling. (Thomson.) The crystallization must take place in a warm situation; for at ordinary temperatures, the simple sulphate crystallizes out even when a large excess of acid is present. (Graham.) Long transparent, four-sided prisms with oblique terminal faces; specific gravity 1·8; taste very acid. The crystals melt at a gentle heat, and if kept fused a long time at 149°, lose nothing of their weight; at a higher temperature they boil, give off water and sulphuric acid, and solidify to a solid crust which fuses again at a stronger heat; and when the heat is still further increased, all the excess of sulphuric acid is given off in the form of sulphurous acid and oxygen gas, 48·5 per cent. of the simple sulphate being left behind. (Thomson.) The crystals continue transparent at 149°; fuse a little above 315°, evolving only a trace of adhering water; and at a higher temperature, yield oil of vitriol (Graham, *Phil. Mag. J.* 6, 331); there remains 48·5 per cent. of the normal salt. (Thomson.) Water resolves this salt into simple sulphate of soda and *hydrated sulphuric* acid with still greater facility

than the corresponding salt of potash. (Graham.) From a solution in 4 parts of hot water, Glauber's salt crystallizes out as it cools. (Brandes & Firnhaber.) Alcohol completely withdraws the second atom of sulphuric acid from the powdered salt. (Brandes & Firnhaber, *Br. Arch.* 7, 173.) (O. Henry and Soubeiran, *J. Pharm.* 11, 437.) The crystals are permanent in the air. (Berzelius.)

According to Link (*Crell. Ann.*, 1796, 1, 27), they deliquesce slowly in the air, and dissolve in 2 parts of cold water.

| | According to Graham. | | | | | Brandes. |
|---|---|---|---|---|---|---|
| NaO | 31·2 | 25·96 | NaO | 31·2 | 22·57 | 22·30 |
| $2SO^3$ | 80·0 | 66·55 | $2SO^3$ | 80·0 | 57·89 | 57·24 |
| HO | 9·0 | 7·49 | 3HO | 27·0 | 19·54 | 20·46 |
| NaO, $2SO^3$ + Aq. | 120·2 | 100·00 | + 3Aq. | 138·2 | 100·00 | 100·00 |

| | According to Thomson. | |
|---|---|---|
| NaO | 31·2 | 21·19 |
| $2SO^3$ | 80·0 | 54·35 |
| 4HO | 36·0 | 24·46 |
| + 4Aq. | 147·2 | 100·00 |

Either the crystals experimented on were of different composition, or some of them must have been analyzed in an impure state.

G. Double Sulphide of Carbon and Sodium and Hydrosulphocarbonate of Soda.—Solution of monosulphide of sodium in water is digested with bisulphide of carbon in a close vessel for some days, at a temperature of 30°, and the liquid evaporated.—Brownish yellow salt, crystallizing only after the solution has been more concentrated; of a cooling, peppery, and afterwards hepatic taste. When perfectly dried and heated to redness in a close vessel, it decomposes, fusing and passing into a mixture of carbon and tersulphide of sodium. It attracts moisture from the air and dissolves readily in water and alcohol. (Berzelius.)

## Sodium and Selenium.

A. Selenite of Soda.—a. *Mono-Selenite.*—Does not crystallize on cooling, but only by evaporation of an aqueous solution in vacuo; it then forms small grains, permanent in the air, which taste like borax, and dissolve very easily in water, but not in alcohol. According to Muspratt, it forms radiated crystals, which fuse without decomposition.

| | Calculation. | | Berzelius. |
|---|---|---|---|
| NaO | 31·2 | 35·78 | 35·5 |
| $SeO^2$ | 56·0 | 64·22 | 64·5 |
| NaO, $SeO^2$ | 87·2 | 100·00 | 100·0 |

b. *Bi-selenite.*—Crystallizes out during the slow cooling of a syrupy solution, in needles united together in tufts, which do not effloresce in the air, but melt when heated, losing their water of crystallization, and forming a liquid which is yellow while hot, and solidifies on cooling to a white mass of a fibrous texture. At a red heat, the salt loses half its acid. Its formula is $NaO, SeO^2 + HO, SeO^2 + 2Aq$.

| | Anhydrous. | | Berzelius. |
|---|---|---|---|
| NaO | 31·2 | 21·79 | 22·17 |
| $2SeO^2$ | 112·0 | 78·21 | 77·83 |
| $NaO, 2SeO^2$ | 143·2 | 100·00 | 100·00 |

| | Crystallized. | | Muspratt. |
|---|---|---|---|
| NaO | 31·2 | 18·24 | |
| $2SeO^2$ | 112·0 | 66·00 | |
| 3Aq. | 27·0 | 15·76 | 15·54 |
| | 170·2 | 100·00 | |

c. *Quadro-selenite.* — Crystallizes by spontaneous evaporation in needles which are permanent in the air. (Berzelius.) Not very deliquescent, and consisting of $NaO, SeO^2 + 3(HO, SeO^2) + Aq$. (Muspratt.)

B. SELENIATE OF SODA.—*Preparation* (II. 240, 1.)—Crystallizes from an aqueous solution at a temperature above 40°, in anhydrous crystals identical in form with those of anhydrous sulphate of soda: *Fig.* 59, sometimes also with the *i*-surface; $a : a^{II} = 134° 22'$; $a : a^{I} = 123° 13'$. Like sulphate of soda, it is most freely soluble in water at 33°. (Mitscherlich, *Pogg.* 17, 138.)

## SODIUM AND IODINE.

A. IODIDE OF SODIUM.—Found in the ashes of marine and littoral plants. Formed by saturating an aqueous solution of hydriodic acid with soda. Crystallizes from this solution, when evaporated at temperatures between 40° and 50°, in anhydrous cubes similar to those of common salt. (Mitscherlich.) Less fusible than iodide of potassium, and solidifies on cooling to a radiated mass of pearly lustre. (Girault.) Not so volatile as iodide of potassium (Gay-Lussac, Girault), but more so than common salt. (Mohr. *Ann. Pharm.* 21, 66.) Loses iodine if fused in the air, soda being formed. (Berzelius.) Heated to redness in the air with charcoal, it is for the most part converted into carbonate of soda, while iodine escapes. In close vessels containing air, it assumes a rose colour, owing to the formation of carbonate of soda and periodide of sodium. (Girault, *J. Pharm.* 27, 390.)

| | Calculation. | |
|---|---|---|
| Na | 23·2 | 15·55 |
| I | 126·0 | 84·45 |
| Na, I | 149·2 | 100·00 |

*Iodide of Sodium with* 4 *Atoms of Water*, or *Hydriodate of Soda with* 3 *Atoms of Water.*—This salt crystallizes at ordinary temperatures from an aqueous solution of iodide of sodium. Large, transparent, longitudinally striated oblique rhombic prisms, belonging to the oblique prismatic system (*Fig.* 87), generally in tables with the *i*-face enlarged. $i : u$ or $u^1 = 109° 48'$; $i$ : the edge between $u^1$ and $u = 113° 12\frac{1}{2}'$; $i : h = 119° 48'$; $i$ : the edge between $h^1$ and $h = 124° 18'$; $i : a = 149° 47\frac{1}{2}'$; $u^1 : u = 118° 32'$; $h : h = 123° 45\frac{1}{2}'$. (Mitscherlich, *Pogg.* 17, 385.) The crystals melt if gently warmed, and on being more strongly heated, leave dry iodide of sodium. (Gay-Lussac.) They do not change so rapidly in vessels *containing* air as the anhydrous salt; the aqueous

solution is also more stable, so that it is not decomposed even by passing a mixture of oxygen and carbonic acid gas through it. The crystals effloresce in dry air, but, like the dry iodide, deliquesce in air moderately charged with moisture. (Girault.) They dissolve in 0·6 parts of cold water (Gay-Lussac), and also in alcohol when not too strong. (Girault.)

| | Calculation. | | Mitscherlich. | Girault. |
|---|---|---|---|---|
| NaI | 149·2 | 80·56 | 80·6 | 76 |
| 4HO | 36·0 | 19·44 | 19·4 | 24 |
| NaI, 4Aq. | 185·2 | 100·00 | 100·0 | 100 |

The crystals used in Girault's experiment, evidently contained mother-liquor still enclosed in them.

B. Aqueous Periodide of Sodium, or Hydriodite of Soda.—Prepared by dissolving iodine in solution of iodide of sodium. Forms a brown solution which gives up its excess of iodine on evaporation much more readily than the corresponding potassium-compound.

C. Di-hypoiodite of Soda?—On heating di-periodate of soda $= 2NaO, IO^7$ to low redness, 6 atoms of oxygen escape, leaving a residue $= 2NaO, IO$, which, on raising the temperature, passes into a mixture of iodide of sodium and soda, with loss of 2 atoms of oxygen. The compound $2NaO, IO$ attracts water from the atmosphere greedily, and iodine is set free on its surface (from absorption of carbonic acid?). It is dissolved with difficulty by cold water. The solution turns reddened litmus paper blue, and bleaches it at the same time. It loses this bleaching property by boiling; because, by this means, the salt is resolved into iodide of sodium, soda, and iodate of soda precipitable by alcohol.

$$3(2NaO, IO) = 3NaO + 2NaI + NaO, IO^5.$$

In boiling water it also dissolves easily, the same decomposition taking place. (Magnus and Ammermüller, *Pogg.* 28, 523.) The same compound remains after heating iodate of soda to low redness, when, if no excess of soda is present, iodine escapes together with the oxygen. (Liebig, *Ann. Pharm.* 27, 43.) If a solution of iodine in caustic soda is evaporated to dryness and exposed to a red-heat, iodine is evolved; and the residue dissolved in water yields crystals, from the aqueous solution of which acids precipitate all the iodine. (Preuss, *Ann. Pharm.* 26, 94.)

D. Iodite of Soda?—Iodine is dissolved in a cold aqueous solution of soda not very highly concentrated (or of carbonate of soda: *Penny*), till it begins to turn brown; the liquid is then left to evaporate in a cold place exposed to the air till it crystallizes. (Mitscherlich.) Prisms of iodate of soda appear first, but afterwards dissolve and are replaced by the crystals of this compound. These crystals are also produced in a few days, by mixing crystallized iodate of soda with a concentrated solution of iodide of sodium in excess. (Penny.) Regular six-sided prisms, perpendicularly truncated; permanent in the air (Mitscherlich); of sharp saline taste; neutral to vegetable colours; efflorescing in the air. (Penny.) The crystals, when heated, evolve a great deal of water at first, and afterwards oxygen with a trace of iodine. (Penny.) A little hot water or cold *alcohol* decomposes the crystals into iodide of sodium which dissolves, *and iodate of soda.* Cold water dissolves them undecomposed. From

this solution, sulphuric and nitric acids precipitate iodine and separate iodic acid; hydrochloric acid behaves in the same manner, but an excess redissolves the iodine, forming with it and the iodic acid, chloride of iodine. (Mitscherlich, *Pogg.* 11, 162; 17, 481.) A lemon-coloured precipitate is produced in the solution by acetate of lead; a light yellow, by nitrate of mercuric oxide; and a yellowish precipitate, by nitrate of silver. It does not turn solution of starch blue. On evaporating the solution, a considerable quantity of iodate of soda, accompanied with but little of the undecomposed compound, crystallizes out. (Penny, *Ann. Pharm.* 37, 202.)

| | | Calculation. | |
|---|---|---|---|
| NaO | 31·2 | | 11·85 |
| $IO^2$ | 142·0 | | 53·95 |
| 10HO | 90·0 | | 34·20 |
| NaO, $IO^2$, 10Aq. | 263·2 | | 100·00 |

| Or, | | | Mitscherlich. |
|---|---|---|---|
| NaI | 149·2 | 28·34 | 29·2 |
| NaO, $IO^5$ | 197·2 | 37·46 | 37·1 |
| 20HO | 180·0 | 34·20 | 33·7 |
| NaI + NaO, $IO^5$ + 20Aq. | 526·4 | 100·00 | 100·0 |

It may therefore be regarded either as a 10-hydrated compound of soda with an iodous acid containing 2 atoms of oxygen, or as a 20-hydrated compound of iodide of sodium with iodate of soda. (Mistcherlich.) According to Penny's analysis, the crystals are = 3NaI + 2NaO, $IO^5$ + 38Aq.

E. Iodate of Soda.—Gay-Lussac distinguished a *basic salt*. This he obtained, sometimes in six-sided prisms, by evaporating a solution of iodine in soda-ley, sometimes in silky needles, by decomposing the iodate of soda dissolved in water, by means of soda. The former crystals are considered by Rammelsberg (*Pogg.* 44, 546) as identical with Mitscherlich's iodite. The latter according to Rammelsberg, are unaltered iodate of soda.

*a.* Mono-iodate.—1. Chlorine gas is passed to saturation through 10 parts of water, containing one part of iodine diffused through it; the liquid is neutralized with carbonate of soda; chlorine again passed through, in order to dissolve the iodine thus thrown down; again neutralized with the carbonate; the iodine which separates again dissolved by means of chlorine; and so on. The liquid is then evaporated to $\frac{1}{10}$ its bulk; mixed, while still warm, with half its volume of alcohol, and the compact crystalline mass consisting of eight-sided prisms which is produced on cooling, is freed from adhering chloride of sodium, by washing with alcohol. (Liebig, *Pogg.* 24, 362.) An excess of carbonate of soda must be avoided; otherwise, di-periodate of soda will be formed. (Magnus & Ammermüller.) The addition of alcohol is unnecessary, as the less soluble iodate can be separated from the common salt by crystallization. (Duflos, *Schw.* 62, 390.)—2. An aqueous solution of terchloride of iodine is incompletely saturated with caustic soda or carbonate of soda; the iodate of soda is then precipitated by alcohol, washed with the same menstruum, and left to crystallize from a solution in water. (Serullas, *Ann. Chim. Phys.* 43, 125.)

The crystals thus obtained yield the anhydrous salt if dried at 150°. (Rammelsberg.) This salt *melts* when heated, and evolves, while still *below redness, 24·45 per cent.* of oxygen together with iodine, leaving

iodide of sodium mixed with soda (Gay-Lussac); according to Liebig, it leaves dihypoiodite of soda; when heated to redness, it yields 24·21 per cent. of oxygen and 75·79 of iodide of sodium. (Benckiser.)—It detonates on glowing charcoal, and slightly when mixed with sulphur and struck. (Gay-Lussac.) With concentrated hydrochloric acid it yields water, chlorine, and a yellow liquid, which probably contains terchloride of iodine and sodium, but does not yield this compound in a crystalline form. (Filhol, *J. Pharm*, 25, 440.) Heated with a small quantity of nitric acid it yields biniodate, and with a larger proportion, teriodate of soda in the anhydrous state. (Penny.) Dissolved hot in a mixture of equal quantities of oil of vitriol and water, it gives by evaporation crystals which when laid upon bibulous paper and nearly dry, become all at once fluid and tenacious. (Liebig.)

It forms crystals with 3 different proportions of water.—¶. Millon (*Ann. Chim. Phys.* 3, 9, 400) obtained crystals of iodate of soda containing under different circumstances 2, 4, 6, 10, 12 and 16 equivalents of water, while Rammelsberg succeeded only in preparing the bihydrate and the decahydrate. ¶.

*α. Bihydrated.*—Obtained by evaporating an aqueous solution in moderately warm air. (Rammelsberg.) By cooling a hot concentrated solution. (Penny.) Forms fine silky needles united together in tufts, which, if the temperature sinks below + 5°, are converted, under the liquid, into the crystals *γ*. At 150° they lose all their water. (Rammelsberg, Penny.)

*β. Sexhydrated.*—Crystallizes on cooling from a more dilute solution in long four-sided prisms. (Penny, *Ann. Pharm.* 37, 203.)

*γ. Decahydrated.*—Obtained by spontaneous evaporation below + 5°. Transparent and colourless. Clear octagonal prisms with six-sided summits, which rapidly change in the air, with loss of 8 atoms of water, into the salt *α*. If this change takes place very slowly, the crystals are converted into a mass of needles of salt *α*. (Rammelsberg, *Pogg.* 44, 548.)

The salt dissolves at 14·5° in 13·8 parts of water: it is insoluble in alcohol. (Gay-Lussac.)

| | Anhydrous. | | | | Bihydrated. | | Rammelsberg. |
|---|---|---|---|---|---|---|---|
| NaO | 31·2 | 15·82 | | NaO | 31·2 | 14·50 | 14·41 |
| $IO^5$ | 166·0 | 84·18 | | $IO^5$ | 166·0 | 77·14 | 77·12 |
| | | | | 2HO | 18·0 | 8·36 | 8·47 |
| NaO, $IO^5$ | 197·2 | 100·00 | | + 2Aq. | 215·2 | 100·00 | 100·00 |

| | Sexhydrated. | | | Decahydrated. | | Rammelsberg. |
|---|---|---|---|---|---|---|
| NaO $IO^5$ | 197·2 | 78·5 | NaO, $IO^5$ | 197·2 | 68·66 | 68·2 |
| 6HO | 54·0 | 21·5 | 10HO | 90·0 | 31·34 | 31·8 |
| + 6Aq. | 251·2 | 100·0 | + 10Aq. | 287·2 | 100·00 | 100·0 |

*b.* Biniodate of Soda.—To an aqueous solution of terchloride of iodine simple iodate of soda is added first, and alcohol afterwards;—the biniodate then falls down. But this salt, if dissolved in water and evaporated, yields crystals of the simple iodate, and an acid mother liquor. (Serullas, *Ann. Chim. Phys.* 45, 59.) By evaporating also a mixture of the iodate with an excess of iodic acid, the simple salt crystallizes out first, and then the iodic acid. (Rammelsberg.) Penny obtained a bin-acid and ter-acid salt, *by treating the simple* iodate with nitric acid (*vid. supra*).

F. Periodate or Hyperiodate of Soda.—*a. Di-periodate.*—1. The same method is employed as in the preparation of the iodate according to Liebig (III., 107), except that an excess of carbonate of soda and chlorine is used, (according to Benckiser, 7 parts of carbonate dried in the air and one part of iodine)—and the solution is evaporated at a temperature near 100°, till the salt separates.—2. Better: Chlorine gas is passed through a warm solution of iodate of soda and caustic soda. The salt is then deposited in a crystalline form, as the concentrated solution cools. At a low red heat it runs together and evolves 10·258 per cent. (3 At.) of water, and 17·895 per cent. (6 At.) of oxygen, leaving dihypoiodite of soda,

$$2NaO, IO^7 + 3HO = 2NaO, IO + 6O + 3HO;$$

afterwards, at a full red heat it evolves 4·767 per cent. more of oxygen [this amounts to only 1·3 atoms, and the loss should really be 2 atoms]; the residue consists of soda and iodide of sodium in equal numbers of atoms. Insoluble in cold, and but slightly in hot water. (Magnus & Ammermüller, *Pogg.* 28, 514.) Dissolves easily in dilute acetic acid, with formation of iodate of soda and formic acid. (Benckiser, *Ann. Pharm.* 17, 254.)

| | Anhydrous. | | |
|---|---|---|---|
| 2NaO | 62·4 | ..... | 25·53 |
| $IO^7$ | 182·0 | ..... | 74·47 |
| $2NaO, IO^7$ | 244·4 | ..... | 100·00 |

| | Crystallized. | | | Magnus & Ammermüller. |
|---|---|---|---|---|
| 2NaO | 62·4 | ..... | 22·99 | ..... 89·74 |
| $IO^7$ | 182·0 | ..... | 67·06 | |
| 3HO | 27·0 | ..... | 9·95 | ..... 10·26 |
| $2NaO, IO^7 + 3Aq.$ | 271·4 | ..... | 100·00 | ..... 100·00 |

b. *Monoperiodate.*—The salt *a* is dissolved in aqueous hyperiodic acid to saturation, and evaporated to the crystallizing point. Colourless crystals permanent in the air, and not containing water. At a red heat it is resolved into 28·754 per cent. of oxygen gas and 71·949 per cent. of iodide of sodium. Readily soluble in water. (Magnus & Ammermüller.)

| | Calculation. | | |
|---|---|---|---|
| NaO | 31·2 | ..... | 14·63 |
| $IO^7$ | 182·0 | ..... | 85·37 |
| $NaO, IO^7$ | 213·2 | ..... | 100·00 |

## Sodium and Bromine.

A. Bromide of Sodium.—1. An aqueous solution of hydrobromic acid is saturated with soda and evaporated at a temperature above 30°. (Mitscherlich, *Pogg.* 17, 385.)—2. Bromide of iron dissolved in water is decomposed by carbonate of soda in atomic proportions—the mixture boiled for a short time—then filtered and evaporated. (O. Henry, *J. Pharm.* 15, 54.)—Crystallizes in cubes. (Mitscherlich.) Tastes rather alkaline than saline. (O. Henry.) Crystallizes from an aqueous solution at ordinary temperatures, in combination with 4 atoms of water, in oblique rhombic prisms which perfectly agree with those of the hydrated iodide of sodium (III., 195). (*Mitscherlich.*) They are pellucid, and fuse

when heated, leaving bromide of sodium. At ordinary temperatures they are permanent in the air. (Mitscherlich.) Readily soluble in water and alcohol. (O. Henry.)

| | Anhydrous. | | | Hydrated. | | Mitscherlich. |
|---|---|---|---|---|---|---|
| Na | 23·2 | 22·83 | NaBr | 101·6 | 73·84 | 73·63 |
| Br | 78·4 | 77·17 | 4HO | 36·0 | 26·16 | 26·37 |
| Na, Br. | 101·6 | 100·00 | NaBr + 4Aq. | 137·6 | 100·00 | 100·00 |

B. Hydrated Perbromide of Sodium or Hydrobromite of Soda. Behaves like the corresponding potash-compound. (Balard.)

C. Hypobromite of Soda.—A small quantity of bromine added to solution of soda, imparts to it bleaching properties which increase with the addition of more bromine; but if an excess be added, the bleaching power is destroyed, owing to the formation of bromate of soda which separates on concentrating the solution. The behaviour of bromine with carbonate of soda is also precisely similar to that described under potash. (Balard.)

D. Bromate of Soda.—Prepared similarly to bromate of potash.—Crystallizes from the aqueous solution at a temperature above 4°, in small anhydrous shining crystals, identical in form with those of bromate of potash (Löwig) and chlorate of soda. (Mitscherlich.) Tetrahedrons with the surfaces of the opposite tetrahedron, the cube, and the rhomboidal dodecahedron. (Rammelsberg, *Pogg.* 52, 85.) The crystals melt when heated, and are converted, with loss of oxygen, into bromide of sodium. They detonate on ignited charcoal, and also by percussion, when mixed with various combustible substances. (Löwig.)

| | Calculation. | |
|---|---|---|
| NaO | 31·2 | 20·86 |
| $BrO^5$ | 118·4 | 79·14 |
| NaO, $BrO^5$ | 149·6 | 100·00 |

Below 4° the salt crystallizes from its solution in long four-sided needles containing water, which effloresce in the air without losing their form. (Löwig, *Mag. Pharm.* 33, 6.)—One part of the anhydrous salt dissolves at 15° in 2·7 parts of water. (Rammelsberg.)

## Sodium and Chlorine.

A. Chloride of Sodium.—*Common salt, Rock-salt, Sea-salt.*—Found in salt beds and in some sandy deserts; in the decrepitating rock-salt of Wielizka, which evolves an inflammable gas when dissolved in water. (Dumas. *Ann. Chim. Phys.* 43, 316; also *Schw.* 59, 486; H. Rose, *Pogg.* 48, 353; *vid.* II., 43.)

Sodium burns at ordinary temperatures in chlorine gas, emitting bright red sparks and forming chloride of sodium. (H. Davy.) With hydrochloric acid gas, sodium and soda behave exactly like potassium and potash.

The salt is obtained:—1. By mechanical extraction from salt-beds.—2. By dissolving impure rock-salt in fresh water, in the water of salt-springs or in sea-water, and then decanting and evaporating.—3. By boiling *down the liquid* from the salt-springs, after it has been concentrated either

by exposure to the air in the *Graduating Works* (*Gradirwerken*) or, more rarely, by partial congelation of the water.—4. By the evaporation of sea-water either in the sun or by artificial heat.—The impurities in common salt—consisting of sulphate of soda, with chloride of calcium and sulphate of lime, chloride of magnesium and sulphate of magnesia, which give it a sharper and more bitter taste,—may be separated by precipitation, first with chloride of barium, and then with carbonate of soda at a high temperature,—then filtering and neutralizing the excess of carbonate of soda with hydrochloric acid. Fuchs (*Kastn. Arch.* 7, 409) precipitates the magnesia from the solution of salt by milk of lime—then the sulphuric acid from the filtrate, by chloride of barium—then filters again—precipitates the lime and baryta by carbonate of ammonia—evaporates the clear liquid to dryness—and exposes the residue to a red heat. Wittstein (*Repert.* 65, 361) proceeds in the same manner, excepting that he uses carbonate of soda instead of ammonia, which precipitates the lime less completely; he then filters and neutralizes the excess of soda by means of hydrochloric acid. The iodide or bromide of sodium possibly present, cannot, however, be separated by either of these methods, but only by repeated crystallization; it then remains in the mother-liquid.

Chloride of sodium crystallizes in cubes, octohedrons, and hollow square pyramids. It is either transparent or translucent. Specific gravity = 2·03 (Unger) 2·078 (Karsten), 2·15 (Kopp). That which has been rapidly crystallized decrepitates in the fire. Common salt fuses at a red heat, and forms a crystalline mass on cooling. At a white heat it volatilizes. It is somewhat less volatile than chloride of potassium; but like that salt, it sublimes at a low-red heat in open, but not in covered crucibles. (H. Rose.) It has a pure saline taste.

| | Calculation. | | Ure. | Longchamp. |
|---|---|---|---|---|
| Na | 23·2 | 39·59 | 39·98 | 39·767 |
| Cl | 35·4 | 60·41 | 60·02 | 60·233 |
| NaCl | 58·6 | 100·00 | 100·00 | 100·000 |

| Or: | Calculation. | | Kirwan. | Berthollet. | Berzelius. | Wieglieb. |
|---|---|---|---|---|---|---|
| NaO | 31·2 | 53·24 | 53 | 53·2 | 53·44 | 53·4 |
| $MuO^2$ | 27·4 | 46·76 | 47 | 46·8 | 46·56 | 46·5 |
| NaO, $MuO^2$ | 58·6 | 100·00 | 100 | 100·0 | 100·00 | 100·0 |

| | Wenzel, Marcet. | Dalton. | Bérard. |
|---|---|---|---|
| NaO | 54 | 56 | 57 |
| $MuO^2$ | 46 | 44 | 43 |
| | 100 | 100 | 100 |

Heated with potassium, it yields chloride of potassium and metallic sodium (H. Davy). Produces a small quantity of sulphide of sodium when mixed in a state of fusion with sulphur. (A. Vogel.) When heated to redness with silica, it yields silicate of soda and hydrochloric acid gas, the decomposition taking place rapidly, if vapour of water has access to the mixture. With oil of vitriol, it gives sulphate of soda and hydrochloric acid gas. According to Berthollet, it also evolves a small quantity of hydrochloric acid gas by distillation with oxalic acid, but not with acetic acid. In solution, it is decomposed by excess of oxide of lead, the products being soda and sub-chloride of lead, $Pb^4Cl$ (Scheele); nitrate of ammonia likewise decomposes it by double affinity. (Karsten.)

*Tetrahydrated Chloride of Sodium*, or *Terhydrated Hydrochlorate of Soda*.—Crystallizes from a saturated solution of common salt in water at — 10°. (Lowitz, *Crell. Ann.* 1793, 1, 314; Fuchs, *Kastn. Arch.* 7, 407.) The crystals begin to form at — 5°. (Nölle, *Ann. Pharm.* 2, 93.)—Large transparent prisms, of the same form and with the same angles as the hydrated iodide of sodium (II., 105). (Mitscherlich, *Pogg.* 17, 385.) According to Hankel (*Pogg.* 53, 623), the *m*-surface is present whilst the *i*-surface is wanting; and $a : m = 111°$; $h : m = 122°$; $\alpha : \alpha = 116\frac{1}{2}$. The crystals effloresce in the air below 0°; the efflorescence begins just above — 10° (Mitscherlich); above 0°, they deliquesce and leave a powder consisting of small cubes. (Fuchs.) They become opaque with the slightest touch of the hand, and then retain their external form even above 0°, whilst internally they are converted into very small cubes. (Manx, *Schw.* 49, 161.)

| | Calculation. | | Mitscherlich. | | Fuchs. | | Löwitz. |
|---|---|---|---|---|---|---|---|
| NaCl | 58·6 | 61·94 | 59·89 | | 54·2 | | 52 |
| 4HO | 36·0 | 38·06 | 40·11 | | 45·8 | | 48 |
| NaCl, 4Aq. | 94·6 | 100·00 | 100·00 | | 100·0 | | 100 |

It is difficult to free the crystals from the whole of the mother-liquid. (Mitscherlich.)

If a dilute solution of common salt is allowed to evaporate at 15° on a glass plate, large six-sided tables of the hydrated salt may be observed by the microscope to crystallize out first; and in these, as the whole becomes drier, small cubes are formed, which increase and gradually absorb all the substance of the tabular crystals; sometimes this transformation takes place quite suddenly. (Ehrenberg, *Pogg.* 46, 240; Frankenheim, *Pogg.* 37, 638.)

*Solution of Chloride of Sodium*.—One part of pure common salt requires, at all temperatures between 0° and 100°, 2·7 parts of water for solution (18 At.) (Fuchs). If the salt is adulterated with chloride of calcium or chloride of magnesium, part of it separates on cooling a solution saturated at a boiling heat: even a solution of these chlorides saturated in the cold precipitates a portion of the salt from a solution of pure chloride of sodium likewise saturated in the cold. (Fuchs.) One part of pure salt dissolves at 14° in 2·78; at 60° in 2·7; and 109·7° in 2·48 parts of water. (Gay-Lussac.) Common salt dissolves in 2·59 parts of cold, and in 2·77 parts of hot water. (Bergman.) Perfectly pure salt dissolves in 2·77 parts of water at 1°, and in 2·56 parts of boiling water; at all events, the deposition of salt from the latter solution takes place only when the liquid is cooled in open vessels—in covered vessels no salt is deposited: the presence of other salts increases its solubility considerably. (Unger, *J. pr. Chem.* 8, 285.) One part of common salt dissolves at 25° in 2·8 parts of water. (Kopp.) One part dissolves in 2·738 parts of water at 18·75°, forming a liquid of specific gravity 1·2046. (Karsten.) The specific gravity of a solution saturated at 8° is 1·205. (Anthon.) At a very low temperature, tasteless ice freezes out of the solution. (Xavier, *Crell. Chem. J.* 1, 212.) Concentrated hydrochloric acid precipitates salt from a saturated solution. Common salt is slightly dissolved by dilute alcohol, but is scarcely soluble in absolute alcohol. ¶. R. Wagner (*J. für pract. Chem.* 40, 448) gives the following table of the solubility of common salt in alcohol of different strengths:

| Per cent. of absol. Al. | Temperature. | Per cent. of salt dissolved. |
|---|---|---|
| 75·0 ..... | 14°·0 ..... | 0·661 |
| ,, ..... | 15°·2 ..... | 0·700 |
| ,, ..... | 38°·0 ..... | 0·736 |
| ,, ..... | 71°·5 ..... | 1·033 |
| 95·5 ..... | 10°·0 ..... | 0·174 |
| ,, ..... | 77°·2 ..... | 0·171 ¶ |

B. Hypochlorite of Soda.—Hitherto obtained only in the state of mixture with chloride of sodium in the so-called *Chloride of Soda*. Chlorine is passed through a solution of soda or carbonate of soda in the proportion of rather less than 1 At. chlorine to 1 At. soda; *e. g.* through a solution of carbonate, till the liquid begins to effervesce strongly: a proof that more than one half of the soda is already combined with chlorine. Labarraque (*J. Chim. Med.* 2, 165) prepares the liquid called after his name, by passing chlorine (evolved from 576 parts of common salt, 448 parts of manganese, 576 parts of oil of vitriol, and 448 parts of water, with the aid of heat) through a solution of 2500 parts of crystallized carbonate of soda in 10,000 parts of water. About half an atom of chlorine only is thus presented to one atom of the carbonate. Payen precipitates chloride of lime in solution with carbonate of soda, and decants the clear liquid from the carbonate of lime thereby produced.

If the current of chlorine gas be stopped just before effervescence begins, a pale yellow liquid is obtained, smelling slightly of chlorine, and having a sharp, biting, saline, but scarcely alkaline taste,—first reddening, and then bleaching turmeric paper. It loses scarcely any of its bleaching power by boiling, but more than half if rapidly evaporated to dryness; less however by slow evaporation. If a given quantity of the liquid be mixed with dilute sulphuric acid, and atmospheric air passed through it as long as chlorine escapes (the chlorine being evolved from the hypochlorous acid and the equivalent quantity of chloride of sodium: $2SO^3 + NaCl + NaO,ClO = 2(NaO,SO^3) + 2Cl$), the residue gives, with a solution of silver, a precipitate, the quantity of which may be assumed = 1 part. [This arises from the small quantity of chloride of sodium, which was formed together with some chlorate of soda.] The same measure of the liquid mixed with solution of silver immediately after adding the dilute sulphuric acid, gives 60 such parts of chloride of silver. [In this case, the silver is precipitated by the chlorine set free from the chloride of sodium and the hypochlorite of soda.] A third such quantity boiled by itself for two hours evolves chlorine, loses a little of its bleaching power, and yields with a solution of silver—after being treated with dilute sulphuric acid, and a current of air passed through—3 parts of chloride of silver. [Thus by the boiling, the quantity of chlorate of soda and the corresponding amount of chloride of sodium is increased threefold.] A similar quantity of the liquid left for 12 days by itself, and then treated as above with dilute acid and a current of air, gives 6 parts of chloride of silver. An equal quantity spontaneously evaporated in the air, leaves crystals consisting almost entirely of carbonate of soda, and not capable of bleaching, even on the addition of sulphuric acid. The residue treated with sulphuric acid and the current of air as before, gives but 1·5 parts of chloride of silver; showing that but little chlorate of soda is produced, and that the greater part of the chlorine escapes during the evaporation. After rapid evaporation, on the contrary, the liquid still retains $\frac{2}{3}$ of its former bleaching power. Carbonic acid gas passed through the liquid carries off but little chlorine, and but slightly affects

its bleaching property; atmospheric air produces still less effect. (Faraday, *N. Quart. J.* 2, 84.) A liquid of this kind boiled down till it becomes covered with a film of salt, yields—besides a mother-liquor containing carbonate of soda—needle-shaped crystals which decolorize solution of indigo. (R. Phillips, *Phil. Mag. Ann.* 1, 376; also *Kastn. Arch.* 11, 211.) When an aqueous solution of carbonate of soda is supersaturated with chlorine gas, a yellow liquid is obtained which bleaches powerfully. If this is evaporated by exposure to the air in a thin stratum, the residue turns turmeric paper brown before it bleaches it,—a proof that, notwithstanding the excess of chlorine, part of the carbonate has remained undecomposed. On boiling, the liquid evolves chlorine,—becomes colourless—and when evaporated leaves chloride of sodium, chlorate of soda, and a small quantity of carbonate. (Faraday.)

If the chlorine, evolved from 10 parts of common salt, 8 parts of peroxide of manganese, and 14 parts of oil of vitriol, is passed into 19 parts of dry powdered carbonate of soda moistened with one part of water only, the bleaching compound is obtained in the solid form, mixed with bicarbonate of soda. (Ph. Mayer & Schindler, *Repert.* 31, 1.)

¶ C. Chlorite of Soda.—Obtained in the same manner as the potash-salt, Deliquescent, but resists the action of heat better than chlorite of potash. In the solid state, it does not decompose below 250°. When raised to that temperature, it first melts, and then turns yellow at the moment of decomposition. (Millon.) ¶

D. Chlorate of Soda.—1. An aqueous solution of caustic soda or carbonate of soda is saturated with chlorine gas, the liquid boiled, and the chlorate of soda separated from the chloride of sodium by crystallization. (Chenevix, Vauquelin.) This separation is more difficult than in the case of potash, because chlorate of soda and chloride of sodium do not differ much in solubility; but by repeated crystallization from alcohol, in which the former dissolves in larger quantity, the separation may be effected to a certain extent. (Chenevix.)—2. Chloric acid is saturated with soda. (Berzelius.)—3. Nine parts of chlorate of potash are boiled with 7 parts of fluoride of silicium and sodium and with water,—then filtered and evaporated to the crystallizing point. (Berzelius.)—4. Bitartrate of soda dissolved in boiling water is decomposed with chlorate of potash—the liquid, when cold, filtered from the crystallized bitartrate of potash,—the latter washed with cold water—the whole then evaporated—and the crystals obtained, freed from adhering cream of tartar by repeated crystallization. (Hopfer de l'Orme, *Mag. Pharm.* 33, 37.) 9½ drachms of crystallized carbonate of soda and 11 dr. 4 gr. of tartaric acid are dissolved in 8 ounces of boiling water; to this is added 1 oz. 16 gr. of chlorate of potash; and the whole digested some time, and left to cool. (Hopfer.) 9 parts of crystallized carbonate of soda and 9½ parts of tartaric acid are dissolved in 48 parts of hot water, and 8 parts of chlorate of potash added; by this means, 7½ parts of chlorate of soda are obtained. (Wittstein, *Repert.* 63, 216.)

Regular tetrahedrons, in which likewise the other four octohedral faces appear, together with the faces of the cube and rhomboidal dodecahedron; isomorphous with bromate of soda. (Mitscherlich, *Pogg.* 17, 388.) It tastes fresh and slightly pungent. (Vauquelin.)

The salt melts in the fire, and (nearly at the same temperature as the potash-salt; *Wächter*) evolves oxygen and chlorine gases; the residue is

decidedly alkaline. On ignited charcoal it detonates rapidly, fusing and emitting a yellowish light. (Vauquelin.) When heated with nitric acid it is decomposed in the same manner as chlorate of potash (II., 61) —into nitrate of soda, perchlorate of soda, and oxygen and chlorine gases. (Penny.) It becomes somewhat moist in the air; requires 3 parts of cold water for solution, and nearly the same quantity of hot water. (Chenevix.) At 16°, it is soluble in 34 parts of alcohol of 83 per cent., and in a smaller quantity of hot alcohol.

| | | Crystallized. | |
|---|---|---|---|
| NaO | 31·2 | | 26·76 |
| $ClO^5$ | 85·4 | | 73·24 |
| NaO, $ClO^5$ | 116·6 | | 100·00 |

E. Perchlorate of Soda.—1. Formed by saturating soda with perchloric acid. (Serullas.)—2. By decomposing chlorate of soda with hot nitric acid. (Penny.) Transparent plates. (Serullas.) Rhomboids. (Penny.) Easily decomposed by heat, but not by hydrochloric acid. (Penny.) Deliquescent. (Serullas, Penny, *Ann. Pharm.* 37, 203; also *J. pr. Chem.* 23, 296.) Soluble also in strong alcohol. (Serullas, *Ann. Chim. Phys.* 46, 297.)

F. Sulphate of Chloride of Sodium.—Prepared like the sulphate of chloride of potassium (III., 63). (H. Rose.)

## Sodium and Fluorine.

A. Fluoride of Sodium.—1. Hydrofluoric acid is saturated with soda, and the solution evaporated to the crystallizing point.—2. 100 parts of fluoride of silicium and sodium are mixed with 112 parts of dry carbonate of soda, and reduced to a thin paste with a small quantity of water. The mixture is then boiled as long as it swells up; and the hard lumpy mass thus obtained is reduced to powder, and again boiled with water till all frothing ceases; the insoluble portion is treated repeatedly with boiling water as long as fluoride of sodium is dissolved out. By this treatment the silica is prevented from assuming the gelatinous form. The fluoride of sodium, on account of its sparing solubility, could not well be extracted from gelatinous silica, a part of which would also dissolve in the water and render the salt impure. The solution is evaporated till it becomes opalescent from the separation of the silica previously dissolved; it is then poured off from the crystals of fluoride of sodium already formed—evaporated by itself—and the residue heated to redness to render the silica insoluble. Gaseous fluoride of silicium escapes during the ignition, if the mother-liquor contains any undecomposed fluoride of silicium and sodium, and may be more effectually got rid of by igniting the residue with carbonate of ammonia in a covered crucible. After this, the mass is dissolved, filtered, and crystallized. All these processes must be carried on in metallic vessels, because glass vessels would be attacked. (Berzelius.)

The salt crystallizes in cubes and octohedrons, which are sometimes clear, sometimes opalescent, and often have a pearly lustre; it decrepitates in the fire, and begins to fuse at a temperature just above the melting-point of glass; its taste is less sharp than that of fluoride of potassium. When mixed with silica, it fuses, without decomposition,

below its own melting-point; on dissolving it in water, the silica remains behind. It is dissolved very slowly by cold water (according to H. Rose, with slight reduction of temperature); 23 parts of water at 16° slowly dissolve one part at most of fluoride of sodium, and no more even with the aid of heat. The solution, when evaporated, again yields crystals of the fluoride, the crystallization being frequently attended with the appearance of light. Alcohol takes up very little of the salt. (Berzelius, *Pogg.* 1, 13; *Vid.* also Gay-Lussac & Thénard, *Recherch.* 2, 21.)

Calculation, according to Berzelius.

| | | | |
|---|---|---|---|
| Na | 23·2 | ..... | 55·37 |
| F | 18·7 | ..... | 44·63 |
| Na, F | 41·9 | ..... | 100·00 |

B. Fluoride of Hydrogen and Sodium.—Fluoride of sodium is supersaturated with hydrofluoric acid, and left to evaporate spontaneously in the air. Small colourless, rhombohedral crystals, having a sharp, purely acid taste. They contain no water. They turn white in the fire, without losing their form, and evolve anhydrous hydrofluoric acid, leaving behind 68·1 per cent. of fluoride of sodium; heated to redness with 6 times their weight of oxide of lead, they give off 14·4 per cent. of water. Rather insoluble in cold, more readily soluble in hot water (as *bi-hydrofluate of soda*); separates again as it cools. (Berzelius, *Pogg.* 1, 13.)

| | Crystallized. | | | Berzelius. |
|---|---|---|---|---|
| NaF | 41·9 | ..... | 68·02 | ..... 68·1 |
| HF | 19·7 | ..... | 31·98 | ..... 31·9 |
| NaF, HF | 61·6 | ..... | 100·00 | ..... 100·0 |

C. Fluoboride of Sodium.—Fluoride of sodium is made to unite with hydrofluate of boracic acid. The salt crystallizes from an aqueous solution, slowly cooled, in transparent, rectangular, four-sided prisms, often shortened and approaching the cubical form. They contain no water; fuse below a red heat; have a bitter, somewhat acid taste; and redden litmus strongly. The compound is changed, by prolonged exposure to heat, into gaseous fluoride of boron which escapes, and fluoride of sodium which remains. It is more soluble in water than the fluoride of hydrogen and sodium, but only slightly soluble in alcohol. (Berzelius.)

## Sodium and Nitrogen.

A. Amide of Sodium.—*Olive-coloured Sodium-compound.* When a quantity of sodium which evolves from water 100 measures of hydrogen gas, is heated in ammoniacal gas, it absorbs tranquilly between 142 and 163 measures, setting 100 measures of hydrogen free, and assuming first a blue and afterwards a green colour. The compound is of an olive-green colour, fuses readily, and exhibits the same relations as the corresponding potassium compound. (Gay-Lussac & Thénard, *Recherch.* 1, 354; *vid.* also Sir H. Davy, *Phil. Transact.* 1810, 24.)

B. Nitrite of Soda.—1. Prepared by heating nitrate of soda to a particular temperature, then dissolving in water, and crystallizing: nitrate

of soda appears first; afterwards the nitrite. (Deiman, Hess.) In the mother-liquor, Deiman (*Scher. J.* 7, 276) thought he had found a compound of soda and nitric oxide. Hess also regarded the crystals which he obtained, not as nitrite of soda, but as soda combined with nitric oxide. (See however, what has been said II. 382, and III. 68.)—2. Solution of soda is saturated with the vapour of hyponitric acid evolved by heating fuming nitric acid. Nitrate of soda is also formed at the same time. (Fritzsche.) Permanent rhombohedrons. Dissolved readily by water, but not by alcohol.

| | Crystallized. | | Hess. |
|---|---|---|---|
| NaO ..... | 31·2 ..... | 45·09 ..... | 44·4 |
| $NO^3$ ..... | 38·0 ..... | 54·91 | |
| NaO, $NO^3$ | 69·2 ..... | 100·00 | |

Hess regards the crystals as composed of 1 atom of soda, 1 atom of nitric oxide, and 1 atom of water, but observes himself that no water is expelled on fusing them.

C. NITRATE OF SODA.—*Rhomboidal Saltpetre, Cubic Nitre, Chili Saltpetre.* Found native in beds several feet in thickness, in the district of Tampa on the borders of Chili and Peru. (Rivero, *Schw.* 34, 450.) Chili saltpetre contains 96·698 per cent. of nitrate of soda, 1·302 per cent. of common salt, 2·0 per cent. of water, with traces of sulphuric acid and lime. (Lecanu, *J. Pharm.* 18, 102.) It contains 99·633 per cent. of nitrate of soda, 0·367 per cent. of common salt, with a trace of lime. (Wittstein, *Repert.* 64, 292.) ¶ Hofsteller (*Ann. Pharm.* 45, 340) gives the following analysis: nitrate of soda 94·291, chloride of calcium 1·990, water 1·993, sulphate of potash 0·239, nitrate of potash 0·426, nitrate of magnesia 0·858, insoluble residue 0·203. ¶ Prepared by saturating carbonate of soda, or distilling common salt, with nitric acid; also by precipitating nitrate of lime with sulphate of soda, and crystallizing. Belongs to the rhombohedral system, its form being an obtuse rhomb (*Fig.* 141); $r : r$ *backwards* $= 106° 30'$; $r : r$ *downwards* $= 73° 30'$; (Brooke, *Ann. Phil.* 21, 452). Sp. gr. = 2·188 (Marx), = 2·20 (Kopp), = 2·2256 (Karsten). It fuses when heated, and on cooling solidifies in a white mass.

| | Crystallized. | Longchamp. | Wenzel. | Richter. | Kirwan. | Dalton. |
|---|---|---|---|---|---|---|
| NaO ..... | 31·2 | 36·6 | 36·75 | 37·5 | 37·9 | 42·34 | 42·4 |
| $NO^3$ ..... | 54·0 | 63·4 | 63·25 | 62·5 | 62·1 | 57·55 | 57·6 |
| NaO, $NO^5$ .... | 85·2 | 100·0 | 100·00 | 100·0 | 100·0 | 99·89 | 100·0 |

When it is heated, pure oxygen gas is evolved at first, and nitrite of soda formed; but afterwards, the oxygen becomes mixed with nitrogen and fumes of hyponitric acid. It detonates less violently with charcoal and other combustible bodies than nitrate of potash. A mixture of 5 parts of nitrate of soda, 1 part of sulphur, and 1 part of charcoal explodes slowly, with a reddish-yellow flame. (Proust, *N. Gehl.* 1, 352.) A detonating powder (III. 70) made with nitrate and carbonate of soda and sulphur, explodes very feebly. (M. Meyer.) When dissolved in water, it is decomposed by sal-ammoniac, by double affinity (Karsten); also by chloride of potassium (Longchamp), and by sulphate of potash (Morveau). Becomes moist only in moist air and deliquesces perfectly, according to Brandes, in an atmosphere saturated with vapour of water. Water dissolves it with great reduction of temperature. One part of the

salt dissolves at −6°, in 1·58; at 0°, in 1·25; and at 119°, in 0·46 parts of water (Marx); it dissolves at 2°, in 2·89; at 28°, in 1·12; and at 47°, in 0·77 parts of water (Osann); at 18·75°, in 1·136 parts of water (Karsten); at 18·5°, in 1·14 parts (Kopp). Sp. gr. of a saturated solution at 18·75° = 1·3769. (*Karsten.*) (From Richter's tables of specific gravity and per centage: *Stoichiometrie*, 3, 164.)

D. Sulphite of Nitric Oxide and Soda.—Similar in properties to the potash-salt, but still more soluble in water. (Pelouze.)

E. Phosphate of Soda and Ammonia.—*Phosphoric salt, Microcosmic salt, Sal microcosmicum, Sal urinæ nativum seu fusibile.* Found in human urine.—1. Five parts of crystallized diphosphate of soda (III. D, *b.* γ) and 2 parts of crystallized diphosphate of ammonia are dissolved in hot water, and then cooled. The mother-liquor, on further evaporation and cooling, yields more crystals; but after each evaporation, the ammonia volatilized must be replaced.—2. From 6 to 7 parts of common diphosphate of soda are dissolved in hot water with 1 part of sal-ammoniac, and the solution filtered and left to cool. (Berzelius.) The salt obtained by this method is contaminated with chloride of sodium. (Wittstein.) If the ordinary phosphate of soda contains pyrophosphate mixed with it, the former alone yields crystals of the phosphate of soda and ammonia when mixed with the sal-ammoniac; the latter crystallizes out by itself. (Winckler, *Repert.* 36, 100.)

Large transparent and colourless prisms, belonging to the oblique prismatic system (*Fig.* 101, 102, and other forms). $i : c = 150° \frac{1}{2}'$; $i : d$ (the face under *c*) $= 123° 28'$; $i : t = 99° 17\frac{1}{2}'$; $i : f$ (backwards) $= 144° 34'$; $i : b$ (forwards) $= 58° 9\frac{1}{2}'$; $d : t = 145° 49'$; $t : b = 138° 52'$; $i : u$ or $u^1 = 93° 4'$; $i : a = 137° 16'$; $a : u = 135° 48'$; $u : u' = 38° 44'$; $u : t = 109° 22'$, &c. (Mitscherlich.) The crystals have a saline, fresh, and somewhat ammoniacal taste. (Proust.) When exposed to the air, they effloresce on the surface and give off ammonia; they melt very easily. The salt, when carefully heated, loses 8 atoms of water, with all the ammonia, leaving $NaO, 2HO, cPO^5$. (Graham.) At a stronger heat it gives off all its water and is converted into simple metaphosphate of soda, $NaO, aPO^5$, having the form of a transparent glass, and amounting, according to Mitscherlich, to 48·71 per cent. In this state, it is used in blow-pipe experiments as a flux for a variety of substances. It dissolves readily in water; the solution, however, loses ammonia when heated.

| | Crystallized. | | | Mitscherlich. | | Riffault. |
|---|---|---|---|---|---|---|
| $NH^3$ | 17·0 | .... | 8·11 | ..... | ..... | 9·000 |
| NaO | 31·2 | .... | 14·89 | ..... | 48·71 ..... | 14·875 |
| $cPO^5$ | 71·4 | .... | 34·06 | ..... | | 34·491 |
| 10HO | 90·0 | .... | 42·94 | ..... | ..... | 41·634 |
| $NH^4O, NaO, HO, cPO^5 + 8Aq.$ | 209·6 | .... | 100·00 | ..... | ..... | 100·000 |

¶ F. Pyrophosphate of Soda and Ammonia.—A solution of acid pyrophosphate of soda is saturated with ammonia, and the liquid evaporated over a mixture of burnt lime and sal-ammoniac. The double salt crystallizes in prisms which appear to belong to the oblique prismatic system. White; readily soluble in water; the solution evolves ammonia when boiled, and afterwards contains acid pyrophosphate of soda.

| | Crystallized. | | | Schwarzenberg. |
|---|---|---|---|---|
| $NH^3$ | 17·0 | .... | 9·79 | 10·18 |
| NaO | 31·2 | .... | 17·97 | 17·70 |
| $bPO^5$ | 71·4 | .... | 41·12 | 40·55 |
| 6HO | 54·0 | .... | 31·12 | 31·57 |
| $NH^4O, NaO, bPO^5 + 5Aq.$ | 173·6 | .... | 100·00 | 100·00 |

(Schwarzenberg, *Ann. Chim. Pharm.* 65, 2.) ¶

G. Sulphate of Soda and Ammonia.—Crystallizes in short prisms; tastes saline and rather bitter. Permanent in the air. Decrepitates when heated, and then swells up, evolving ammonia and acid sulphate of ammonia, and leaving sulphate of soda. (Link, *Crell. Ann.* 1796, 1, 30; Seguin, *Ann. Chim.* 91, 219; Riffault, *Ann. Chim. Phys.* 20, 432; also *Schw.* 36, 423.)

| | Crystallized. | | | Riffault. |
|---|---|---|---|---|
| $NH^3$ | 17·0 | .... | 9·82 | 9·678 |
| NaO | 31·2 | .... | 18·01 | 18·550 |
| $2SO^3$ | 80·0 | .... | 46·19 | 45·740 |
| 5HO | 45·0 | .... | 25·98 | 26·032 |
| $NH^4O, NaO, 2SO^3 + 4Aq.$ | 173·2 | .... | 100·00 | 100·000 |

## Sodium and Potassium.

A. Alloy of Sodium and Potassium.—These two metals unite readily. One part of sodium forms, with from ½ to 10 parts of potassium, a compound which remains fluid at 0°; when too much sodium is used, the alloy becomes brittle and crystalline. An alloy of 1 part of sodium and 10 parts of potassium floats on rock-oil. (According to Böttger, however, *J. pr. Chem.* 1, 303, it does not.) In all these alloys, the potassium becomes oxidized first. (Gay-Lussac & Thénard.)

B. Carbonate of Soda and Potash.—A mixture of 1 atom of carbonate of potash and 1 atom of carbonate of soda, fuses much sooner than either of these salts alone. (Mitscherlich, *Pogg.* 14, 189.)

¶ According to Marguerite (*J. de Pharm. & Chim.* 7, 344, *Ann. Pharm.* 56, 220), a double carbonate of potash and soda is obtained by the repeated concentration and crystallization of the mother-liquor of ferrocyanide of potassium; or more directly by dissolving carbonate of soda with excess of carbonate of potash and concentrating. The salt forms slender, very soluble crystals which melt in their own water of crystallization at 40°, and effloresce in vacuo; in the air they undergo scarcely any alteration. By recrystallization the salt is decomposed. It readily crystallizes, however, without alteration from a saturated solution of carbonate of potash. The formula of the salt is $2(NaO, CO^2) + KO, CO^2 + 18$ Aq. ¶

C. Phosphate of Soda and Potash.—Ordinary monophosphate of potash is neutralized with carbonate of soda and left to crystallize. The compound salt crystallizes out perfectly in combination with water. Crystalline system, the oblique prismatic (*Fig.* 107, 108, and other forms); $i : t = 96° 21'$; $i : u$ or $u^1 = 94° 1'$; $i : a = 122° 27'$; $i : h$ *backwards* $= 116° 27'$; $u : u^1 = 78° 40'$; $u : t = 129° 20'$; $z : z = 117° 14'$; $u^1 : m = 140° 40'$ and so on. (Mitscherlich.)

| | Crystallized. | | | Mitscherlich. |
|---|---|---|---|---|
| KO | 47·2 | .... | 15·59 | |
| NaO | 31·2 | .... | 10·30 | ..... 49·6 |
| $cPO^5$ | 71.4 | .... | 23·58 | |
| 17HO | 153·0 | .... | 50·53 | ..... 50·4 |
| KO, NaO, HO, $cPO^5$ + 16Aq. | 302·8 | .... | 100·00 | ..... 100·0 |

¶ D. Pyrophosphate of Soda and Potash.—When a solution of the acid pyrophosphate of soda is saturated with carbonate of potash and the liquid concentrated to a thin syrup, the whole solidifies on cooling to a mass of fine acicular crystals which appear to belong to the oblique prismatic system. The salt is white and transparent; the solution has an alkaline reaction.

| | Calculation. | | | |
|---|---|---|---|---|
| KO | 47·2 | .... | 18·30 | ..... 18·18 |
| NaO | 31·2 | .... | 12·10 | ..... 12·08 |
| $bPO^5$ | 71·4 | .... | 27·71 | ..... 27·64 |
| 12HO | 108·0 | .... | 41·89 | ..... 42·10 |
| KO, NaO, $bPO^5$ + 12Aq. | 257·8 | .... | 100·00 | ..... 100·00 |

(A. Schwarzenberg, *Ann. Chim. & Pharm.* 65, 2.) ¶

E. Sulphate of Soda and Potash.—A mixture of the sulphates of potash and soda in equal numbers of atoms fuses much more readily than sulphate of potash alone. The mass is glassy when cold and while cooling cracks in many places, without however emitting light; at the same time it becomes brittle but not crystalline. When it is dissolved in hot water and boiled, no sulphate of soda separates from it; but as it cools, light is emitted, and anhydrous crystals are produced, having the form of sulphate of potash, and containing from 1½ to 2 atoms of sulphate of potash with 1 atom of sulphate of soda. Sometimes a salt rich in soda is formed under the same circumstances; in that case, no emission of light is observed.

Also by melting together sulphate of potash and common salt, a mass is obtained, which, from a hot solution, deposits the same crystals free from chlorine, and with emission of light. 2 atoms of sulphate of soda and 3 atoms of sulphate of potash fuse with difficulty to a mass which becomes very much broken up as it cools, and emits very little light on crystallizing from a solution in hot water. (H. Rose, *Pogg.* 52, 452; *vid.* also I., 207.)

When 1 atom of *seleniate of potash* is melted with 1 atom of *sulphate of soda*, and the mass dissolved in hot water, crystals similar to those of sulphate of potash are formed, with vivid emission of light, as the liquid cools; they decrepitate when heated, and contain 41·38 per cent. of potash, 9·51 of soda, 4·84 of selenic acid, and 44·68 of sulphuric acid. (H. Rose, *Pogg.* 52, 588.)

F. Nitrate of Soda and Potash?—A solution of 1 part of nitrate of potash and 1 part of nitrate of soda in 3 parts of boiling water, yields as the liquid cools, long, silky needles, united together in stellated groups. (Loose, *Pharm. Centralblatt*, 1837, 505.)

### Sodium and Sodium.

A. & B. The compounds obtained by fusing one atom of common salt with 1 atom of carbonate, or with 1 atom of sulphate of soda, exhibit properties similar to those of the corresponding potash-compounds. (III., 71, B. & C.) (Döbereiner.)

C. Compound of Chloride of Sodium with Iodate of Soda.—1. When iodate of soda is prepared from chloride of iodine and carbonate of soda (III., 107), the liquid, on evaporation, first deposits pure iodate of soda; afterwards, at a higher temperature and greater degree of concentration, the iodate of soda crystallizes out combined with common salt.—2. When a tolerably large quantity of solution of caustic soda is added to an aqueous solution of iodate of soda, and chlorine gas passed through the liquid till no more diperiodate of soda falls down, chloride of sodium crystallizes from the decanted liquid, first combined with iodate of soda, then by itself, and afterwards mixed with chlorate of soda.

Transparent four-sided prisms, permanent in the air, often having a tabular form in consequence of the greater size of the two lateral faces. —The crystals when heated become opaque, lose their water, and fuse to a clear liquid, which evolves nothing but oxygen gas, and, after exposure to a very powerful heat, leaves a mixture of chloride and iodide of sodium. In cold water—which withdraws the common salt—the crystals are converted into an opaque mass of needles united in tufts, and consisting of iodate of soda with 2 atoms of water. (Rammelsberg, *Pogg.* 44, 548.)

| | Crystallized. | | Rammelsberg. |
|---|---|---|---|
| 2NaCl | 117·2 | 27·75 | 27·15 |
| $NaO, IO^5$ | 197·2 | 46·68 | 47·50 |
| 12HO | 108·0 | 25·57 | 25·05 |
| $2NaCl + NaO, IO^5 + 12Aq$ | 422·4 | 100·00 | 99·70 |

### Other Compounds of Sodium.

With many of the metals—namely, with arsenic, antimony, tellurium, bismuth, zinc, tin, lead, copper and mercury.

## Chapter III.

# LITHIUM.

Arfvedson. *Schw.* 22, 93; also, *Ann. Chim. Phys.* 10, 82; further, *Schw.* 34, 214.
Vauquelin. *Ann. Chim. Phys.* 7, 284; also *Schw.* 21, 397.
C. G. Gmelin. *Gilb.* 62, 399; 64, 371, and *Schw.* 30, 173.
Kralovanszky. *Schw.* 54, 230 and 346.
R. Hermann. *Pogg.* 15, 480.

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*History.* The oxide of Lithium was discovered in 1817, by Arfvedson, in the laboratory of Berzelius.

*Sources.* As oxide, in the inorganic kingdom only (hence its name); principally in petalite (5 per cent.), lithiaspodumene (8 per cent.), amblygonite (11 per cent.), triphyline (3·4 per cent.), lepidolite (3·6 per cent.), lithia mica, apyrite and the tourmaline of Utön. Also in very small quantity in the mineral waters of Karlsbad, Franzbad, and Marienbad (Berzelius, *Schw.* 44, 127; *Pogg.* 4, 248); in the water of Pyrmont (Brandes, *Schw.* 45, 369); in the mineral water of Hofgeismar (Wurzer, *Schw.* 46, 121); in the salt spring of Kissingen (Fuchs & Fickentscher, *J. pr. Chem.* 5, 321); in the goître-water of Hall in Austria (Holger, *Zeitschr. Phys. Math.* 9, 75); in the mineral waters of Mönchsofen (Buchner. *Repert.* 23, 221); of Bilin (Reuss); of Klausen in Steiermark (Holger); of Hohenstein (Reichel); of Kreuznach (Löwig); of Lavey near Bex (Baup); and of Slintsch in Hungary (Wagner).

According to Brandes (*Scher. Ann.* 8, 120) a white combustible metal is obtained from lithia, when placed in the circuit of a voltaic battery.—Kralovanszky was unable to reduce the metal from the oxide by means of iron, charcoal, or potassium.

*Atomic weight of Lithium* (H = 1) = 6·4264 (Berzelius, *Pogg.* 17, 379); = 6·084. (R. Hermann, *Pogg.* 15, 480.)

### *Compounds of Lithium.*

### Lithium and Oxygen.

### A. Lithia. LO.

*Oxide of Lithium.* Not yet known in the free state.

Calculation, according to Berzelius.

| | | |
|---|---|---|
| L | 6·4 | 44·44 |
| O | 8·0 | 55·56 |
| LO | 14·4 | 100·00 |

LO = 80·33 + 100 = 180,33. Berzelius.)

*Combinations.—a.* With water. *a.* HYDRATE OF LITHIA.

*Preparation.*—1. *Petalite* in powder is heated to redness with 4 parts of carbonate (or nitrate) of baryta; the mass is then dissolved in dilute hydrochloric acid; evaporated to dryness; again treated with water acidulated with hydrochloric acid; the liquid separated from the silica by filtration; the baryta precipitated by excess of sulphuric acid, and the alumina by carbonate of ammonia. The solution is then evaporated to dryness, and the ammonia expelled by ignition; whereupon, sulphate of lithia remains, together with a small quantity of sulphate of lime (and manganese). The residue is dissolved in water, and the sulphuric acid precipitated by means of acetate of baryta (if manganese be present, it must be first separated with sulphide of ammonium and the solution evaporated to dryness, exposed to a red heat, and then re-dissolved in water). The liquid separated from the precipitate and containing the acetates of lithia, baryta, and lime, is evaporated; the residue heated to redness; and the ignited mass powdered, and exhausted with boiling water as long as any alkaline matter is dissolved out. The solution of carbonate of lithia thus obtained is evaporated (to a small bulk, whereupon the carbonate of lithia separates, leaving in the liquid any carbonate of potash or soda that may be present); the residue boiled with water and excess of hydrate of lime for several hours, and stirred; after which it is filtered, evaporated, and fused in a silver crucible. (Arfvedson.) [The additions put between brackets are made by C. G. Gmelin.]

2. To save baryta, the elutriated powder of *Spodumene* or *Petalite* is intimately mixed with twice its weight of quick-lime; the mixture strongly ignited for a considerable time in a Hessian crucible; the product dissolved in hydrochloric acid; the solution mixed with sulphuric acid, evaporated to dryness, and the excess of sulphuric acid expelled by exposure to a strong heat; and the dry residue powdered, exhausted with water, and strained through linen, on which most of the gypsum is retained: this must be repeatedly washed and pressed. Alumina is precipitated from the filtered liquid by carbonate of ammonia, or by digestion with carbonate of lime. The lime is afterwards removed from the filtrate either by throwing it down with oxalate of ammonia, filtering, evaporating, and heating to redness, after which sulphate of lithia is left behind (Berzelius, *Lehrbuch*); or by evaporating the filtrate to dryness; exposing the residue to a red heat; then exhausting with water, which leaves the greater part of the gypsum behind; precipitating with acetate of baryta; filtering, evaporating, and heating to redness; and lastly boiling the powdered mass with water, which dissolves the carbonate of lithia, and leaves behind the carbonates of baryta, lime, and magnesia (present in the lime used). The water takes up a small quantity of the carbonate of magnesia; but by saturating with sulphuric acid and crystallizing, pure sulphate of lithia is obtained, and this can be converted into pure lithia as in No. 9 (Arfvedson). Berthier (*Ann. Chim. Phys.* 59, 189) mixes in a charcoal crucible one part of *spodumene* with 1·09 parts of carbonate of lime, and subjects the mixture to an intense heat till it fuses to a glass; and after reducing it to powder, exhausts it with sulphuric acid: this process yields 0·192 parts of sulphate of lithia.

3. An intimate mixture of one part of *spodumene* and 2 parts of litharge is reduced to perfect fusion at a strong red heat; then poured out; and the glass finely powdered, and dissolved in weak nitric acid, which separates the silica. The oxide of lead is then precipitat[illegible] by sulphuric acid; the filtrate evaporated to dryness; the residue d[illegible]lved

in water; lime and magnesia separated by means of carbonate of ammonia; the liquid filtered and evaporated; and the dry mass heated in a porcelain crucible. The residue is sulphate of lithia. (Quesneville, *J. Pharm.* 16, 164; also *N. Tr.* 22, 1, 257.)

4. A mixture of finely powdered *spodumene* and charcoal is heated to redness in a porcelain tube, with a current of chlorine gas passing over it. Decomposition ensues readily; and from the residue, when cold, water dissolves out chloride of lithium. (*Setterberg*, 38, 480.)

5. A mixture of 1 part of *Lepidolite* and 2 parts of lime is heated for two hours at a strong red heat; the greyish white mass broken up and reduced with water to a thin paste; dilute sulphuric acid added in small portions at a time, till the liquid becomes slightly acid; more water added; and the whole thrown upon a filter and washed. The filtrate thus freed from gypsum is then partly evaporated, and separated from lime, alumina, iron, and manganese by means of carbonate of soda. It is afterwards further evaporated, and carbonate of lithia precipitated from the boiling concentrated solution, by a solution of carbonate of soda in twice its weight of water (a further quantity of lithia may be separated from the mother-liquor by means of phosphate of soda): the precipitated carbonate of lithia dissolved in weak hydrochloric acid gives with carbonate of ammonia, a precipitate of pure carbonate of lithia. The supernatant liquid yields with carbonate of ammonia, after further evaporation, a small quantity more; and if again evaporated and heated to low redness, it yields impure chloride of lithium, mixed with more or less carbonate of lithia. (Werner, *J. Pr. Chem.* 12, 55.)

6. One part of *lepidolite* in powder is heated with 2 parts of slaked lime at a moderate red heat for two hours; and the powdered mass, after being made into a paste with water, is left in a warm place by itself for three months. By this treatment, nearly all the lithia and potash are set at liberty, and are found partly dissolved in the water, and partly retained in the hardened mass. This mass is boiled with water after being reduced to powder; the filtrate saturated with carbonic acid gas, and evaporated to dryness; and the carbonate of potash dissolved out from the carbonate of lithia by means of water containing alcohol. The insoluble matter once more heated with lime and treated as above, sometimes yields an additional quantity of lithia. (Fuchs, *J. pr. Chem.* 5, 320.)

7. In operating on the large scale, 1 part of powdered *lepidolite* is heated in a reverberatory furnace with 2 parts of lime, slaked and reduced to powder by water, the heat being continued till the whole cakes together. The powdered mass is then mixed with half its weight of lime; reduced to a paste with water; boiled for a long time, the water being replaced as it evaporates; decanted; the residue again boiled with water and $\frac{1}{10}$ part of lime; then decanted and washed. The two liquids containing lithia and potash, with a small quantity of lime, alumina, and heavy metallic oxides, are mixed, after filtration; then saturated with hydrochloric acid and evaporated; the lime and alumina precipitated by carbonate of ammonia; potash added to the filtrate as long as it causes turbidity; the liquid filtered; the metallic oxides thrown down by sulphuretted hydrogen; the solution again filtered and evaporated to dryness; the residue heated sufficiently to destroy organic matter; then dissolved in water, neutralized with hydrochloric acid; filtered; evaporated to dryness; and the chloride of lithium dissolved out by absolute alcohol, which leaves the chloride of potassium untouched. (Mitscherlich, *Lehrbuch*, 2, 85.)

8. A mixture of 7 parts of powdered *lepidolite* and 2 parts of calcined

green vitriol is heated gently for some time, so that it may not fuse but merely cake together; the powdered mass is exhausted with water; the filtrate freed from alumina, iron, and manganese, by sulphide of ammonium; the filtered liquid evaporated to dryness; the sulphate of ammonia expelled at a moderate heat; the residue, consisting of the sulphates of potash and lithia, reduced to powder; and the latter salt separated by a moderate quantity of water mixed with alcohol. If this solution still contains sulphate of potash, the sulphate of lithia must be purified by crystallization. (Fuchs.)

9. Powdered *lepidolite* is boiled for a long time with oil of vitriol; the mass exhausted with water, filtered, and evaporated; the earths precipitated by carbonate of ammonia; and manganese by sulphide of ammonium, the excess of which is decomposed by boiling. The sulphuric acid is then precipitated by acetate of baryta; the liquid filtered and evaporated to dryness; the mass heated to redness, boiled with water, filtered, and again evaporated to dryness; the carbonate of potash taken up with a small quantity of cold water; and the undissolved carbonate of lithia treated as in the first method, or else saturated with sulphuric acid and baryta water added to the liquid as long as it produces a precipitate of sulphate of baryta, excess of baryta being carefully avoided. The filtrate is then distilled in a retort to separate the water, whereupon crystals appear, which are afterwards fused. (C. G. Gmelin.) In applying this method on the large scale, the lepidolite is boiled with the oil of vitriol in earthen pans, and stirred with earthenware rods till it is dry. The mass is then boiled with water in a clean copper vessel; the filtrate evaporated to dryness; the residue dissolved in water; the earths precipitated by carbonate of ammonia; the liquid evaporated again as before; and the sulphate of ammonia driven off by heating in glass vessels. The vessels are then broken; the cake of salt dissolved in water; the sulphuric acid thrown down by acetate of lead; the lead separated from the filtrate by hydrosulphuric acid; the liquid again filtered, evaporated to dryness, and the residue dissolved in water; the rest of the sulphuric acid separated by acetate of lead, and the lead precipitated as before. The solution is then filtered and evaporated; the residue heated in a copper crucible; the fused cake of carbonate of lithia and carbonate of potash dissolved in water; the solution filtered from oxide of copper; and the filtrate so far evaporated in a copper pan, that carbonate of lithia crystallizes out on cooling: finally, the remaining mother-liquor is evaporated to dryness, and the carbonate of potash separated by cold water. (Joss, *J. Pr. Chem.*, 1, 139.)

10. Very finely powdered *petalite, spodumene, apyrite,* or *lepidolite,* is digested for some days with oil of vitriol; then evaporated to dryness; the remainder boiled repeatedly with water and filtered; and the alumina precipitated by carbonate of ammonia. The clear liquid after filtration is evaporated; and the residue heated to redness, and further proceeded with, as in the first method, with acetate of baryta, exposure to a red heat, &c. (Berzelius.)

11. *Triphyline* is dissolved in hydrochloric acid; the protoxide of iron converted into sesquioxide by boiling with a little nitric acid; the phosphate of iron precipitated by ammonia; the protoxide of manganese by sulphide of ammonium; the filtered liquid evaporated to dryness; and the ammoniacal salts expelled by heat. The residue consists of soluble chloride of lithium. (Fuchs. *J. pr. Chem.* 5, 319.) The chloride may be converted into sulphate of lithia by heating it with sulphuric acid; and from

the sulphate, caustic lithia is obtained by treating it with baryta. Lithia prepared by this method often retains magnesia.

*Properties.* White, transparent; fuses at a temperature below redness, and does not appear to volatilize at a white heat. (C. Gmelin.) Has a crystalline fracture; and the same taste, causticity, and alkaline effect on vegetable colours, as potash and soda. (Arfvedson.)

*β.* Crystallized Lithia.—Separates in small grains from an aqueous solution during evaporation. (C. Gmelin.)

*γ.* Solution of Lithia.—Hydrate of lithia does not deliquesce in the air (Arfvedson); it dissolves in water with elevation of temperature. Lithia is much less soluble in water than potash or soda, and apparently not more soluble in hot than in cold water. (C. Gmelin.)

*b.* With acids lithia forms the Lithia-salts. These are white when the acid itself is colourless; they are more readily fusible than the corresponding salts of potash and soda; and are permanent in the fire, if the acid is not too volatile or easily decomposed. Fused with carbonate of soda on platinum foil, they produce a dark yellow stain round the circumference, whereas carbonate of soda by itself produces this effect in a much smaller degree only. (Berzelius.) Fused on platinum wire, they impart a carmine colour to the blowpipe flame. An excess of potash-salt does not interfere with the production of this colour, but the presence of a small quantity of soda gives rise to the yellow flame. (H. Rose.) ¶ Stein (*J. für prakt. Chem.* 31, 361; *Ann. Pharm.* 52, 243, 1844) has observed that this latter effect is produced when too strong a heat is applied; and that if the lithia salt is barely fused on a platinum wire, saturated with talc, and then heated in the flame of a candle, the red colour is discernible with one part of lithia to 2580 parts of soda. ¶

Alcohol, in which a salt of lithia is dissolved or diffused in the state of fine powder, also burns with a carmine-coloured flame. (C. Gmelin.) The same occurs also with paper saturated with a solution of a salt of lithia, or the wick of a taper saturated with moistened phosphate or acetate of lithia. (Turner, *Ed. Phil. J. of Sc.* 2, 267; 4, 113; also *Schw.* 47, 41.) All the lithia salts are soluble in water; but the carbonate phosphate, and the phosphate of lithia and soda difficultly so. Hence the other salts of lithia, when not dissolved in too much water, yield difficultly soluble precipitates with carbonate of ammonia, potash, or soda, and with phosphate of soda. Carbonate of soda precipitates the salts of lithia after some time only. Common diphosphate of soda does not precipitate them in the cold, even after a long time, except on the addition of ammonia, which gradually gives rise to an abundant precipitate. But a mixture of a salt of lithia with phosphate of soda, becomes turbid by boiling or evaporation,—and the dry residue, on being treated with water, leaves the difficultly soluble phosphate of lithia and soda.

A solution of a salt, which is not clouded by caustic soda in the cold, or by carbonate of soda at a boiling heat, but yields with phosphate of soda on evaporation, an almost insoluble white powder, contains lithia. The detection and separation of lithia are founded on this property. (Berzelius.)

Phosphate of potash gives no precipitate, even on boiling or evaporation; but on the addition of ammonia, an abundant precipitate after some time. (H. Rose.) Hydrofluosilicic acid throws down from salts of lithia the almost insoluble fluoride of silicium and lithium (Berzelius); and carbazotic acid, throws down carbazotate of lithia. (H. Rose, *Analyt.*

*Chem.*)—The concentrated solution of a salt of lithia is not precipitated by perchloric acid (Serullas), sulphate of alumina (C. Gmelin), bichloride of platinum, oxalic acid, or tartaric acid. (Arfvedson, C. Gmelin.)

*c.* With earths, in the above named minerals, excepting triphyline. All minerals containing lithia impart a purple colour to the blow-pipe flame, provided they are fusible. This colour is rendered much more distinct when the mineral is mixed with one part of double fluoride of potassium and hydrogen and 4½ parts of bisulphate of potash, and exposed to the blowpipe flame on platinum wire. (Turner.) The same minerals, when mixed with a small quantity of a mixture of one part of fluorspar and one part of sal-ammoniac, impart a greenish tint at first, and afterwards a red colour to the flame. (Berzelius.)—*d.* Lithia is but sparingly soluble in alcohol, which partly precipitates it from an aqueous solution. (C. Gmelin.)

### B. Peroxide of Lithium.

The hydrate and the carbonate of lithia when heated in the air, appear to be partly converted into peroxide, which has not yet been prepared in the pure state, but has a great proneness to induce oxidation in platinum, probably producing a compound of lithia with oxide of platinum. No alkali attacks a platinum crucible in which it is ignited, so severely as lithia and its carbonate, which cover the surface of the platinum with a dark-yellow or olive-green colour. (Berzelius.) Silver is also corroded and dissolved by carbonate of lithia in a state of fusion. (Kralovanszky.)

### Lithium and Carbon.

Carbonate of Lithia.—*a. Monocarbonate.*—The transparent hydrate of lithia becomes opaque in the air from absorption of carbonic acid. (C. Gmelin.)—1. Sulphate of lithia is precipitated by acetate of baryta, the liquid filtered and evaporated, and the acetate of lithia decomposed by exposure to heat.—2. An excess of carbonate of ammonia is dissolved in a concentrated solution of chloride of lithium, and the carbonate of lithia, which is almost entirely precipitated, is washed on a filter with alcohol. (Berzelius.)—The salt is white, fuses at a low red heat (Arfvedson) to a clear liquid (Hermann), and solidifies on cooling to a vitreous mass (Arfvedson); this mass is crystalline (Turner), transparent, and separates into pieces which have a pearly lustre. (Hermann, *Pogg.* 15, 480.) It has a slight but distinctly alkaline taste, and turns reddened litmus paper blue. (Arfvedson.) A solution of one part of carbonate of lithia in 1000 parts of water still exhibits an alkaline reaction. (C. Gmelin.)

| | Calculation. | | Hermann. | Schaffgotsch. | C. Gmelin. | Kralovanszky. |
|---|---|---|---|---|---|---|
| LO ..... | 14·4 | 39·56 | 39 | 39·83 | 45·54 | 45·8 |
| $CO^2$ ..... | 22·0 | 60·44 | 61 | 60·17 | 54·46 | 54·2 |
| LO, $CO^2$ | 36·4 | 100·00 | 100 | 100·00 | 100·00 | 100·0 |

Crystallizes by slow evaporation in small prisms, which effloresce slightly in the air (Arfvedson) in pearly cubes. (Kralovanszky.)—The fused salt is dissolved with great difficulty by water, but more easily when

powdered, especially if the water is hot. One part of carbonate of lithia requires 100 parts of cold water for solution. Carbonate of lithia gives up its acid to baryta and lime; it decomposes the salts of ammonia, lime, magnesia, alumina, iron, copper, and silver. (Vauquelin.) It is insoluble in alcohol. (C. Gmelin.)

*b. Acid-salt.*—Water saturated with carbonate of lithia dissolves an additional portion when carbonic acid is passed through it. The solution yields, on evaporation, a crystalline crust of salt which decrepitates strongly in the fire. (Arfvedson.) According to C. Gmelin, the excess of carbonic acid escapes on evaporation, and the simple salt is thrown down.

### Lithium and Boron.

Borate of Lithia.—*a. Biborate.*—According to Arfvedson, this salt forms crystals which have an alkaline taste and reaction; swell up and lose their water of crystallization when heated; and fuse to a transparent glass: they are easily soluble in water. According to C. Gmelin, it forms a transparent gummy mass.

*b. Acid-Salt.*—Indistinctly crystalline, and less easily soluble in water than *a*. (C. Gmelin.)

### Lithium and Phosphorus.

Phosphate of Lithia.—*a. Diphosphate.*—Precipitated from an aqueous solution of carbonate of lithia on the addition of phosphoric acid and application of heat, the carbonic acid escaping; precipitated from sulphate of lithia by phosphate of ammonia, but not by phosphoric acid (C. Gmelin); from the acetate, on the contrary, it is almost completely precipitated by phosphoric acid. (Berzelius.) White, bulky powder, nearly insoluble in water. (C. Gmelin.)

*b. Monophosphate.*—Crystallizes in transparent grains on the slow evaporation of the aqueous solution; readily soluble in water. (C. Gmelin.)

### Lithium and Sulphur.

A. Monosulphide of Lithium.—Formed by heating sulphate of lithia to redness in a retort with charcoal. The charcoal must not predominate, otherwise a pyrophoric mass will be formed. The sulphide dissolves in water and alcohol more readily than the hydrate of lithia. (Berzelius.)

B. Sulphide of Lithium and Hydrogen.—Formed when sulphuretted hydrogen gas is passed over ignited carbonate of lithia. The resulting mass is pale-yellow in the cold, becomes dark-brown when heated, and fuses at a higher temperature. (Berzelius.)

*Hydrated Sulphide of Lithium and Hydrogen*, or *Bi-hydrosulphate of Lithia.*—A solution of A is saturated with sulphuretted hydrogen gas. The colourless liquid evaporated in a retort to the consistence of syrup, deposits crystals of carbonate of lithia, accidentally formed; and if afterwards left to evaporate in vacuo, over fused potash, it yields a confused

mass of salt, which becomes moist in the air, and is readily dissolved by alcohol. The aqueous solution evaporated in the air yields long prisms, which correspond to the *hydrated bisulphide of lithium.* (Berzelius, *Pogg.* 6, 439.)

C. PERSULPHIDE OF LITHIUM.—When hydrate of lithia is fused with sulphur, a yellow mass is obtained, which is soluble in water and behaves with acids like other livers of sulphur. (Vauquelin.)

¶ D. SULPHITE OF LITHIA.—$LO, SO^2 + 6Aq$.—Obtained by passing sulphureous acid gas through water in which carbonate of lithia is suspended. White, feathery crystals. (Danson, *Qu. J. of Chem. Soc.* 2, 207.)

E. HYPOSULPHATE OF LITHIA.—$LO, S^2O^5 + 2Aq$. Forms indistinct crystals, deliquesces in the air, and is partially soluble in alcohol. (Rammelsberg, *Pogg.* 66, 79.) ¶

F. SULPHATE OF LITHIA.—a. *Simple salt.—Preparation.* Already given with that of the hydrate of lithia. The excess of sulphuric acid possibly occurring in any of the methods, may be removed by neutralizing with ammonia and igniting. White mass; fuses with difficulty, unless gypsum is present; but then, even if the quantity of gypsum be small, it melts below a red heat. Has a pure saline taste without bitterness. (Arfvedson.)

| | Anhydrous. | | Hermann. | Pleischl. | C. Gmelin. | Vauquelin. | Kralovanszky. | Arfvedson. |
|---|---|---|---|---|---|---|---|---|
| LO ..... | 14·4 | 26·47 | 26·0 | 26·6 | 27·94 | 30·8 | 31·1 | 31·59 |
| $SO^3$ ..... | 40·0 | 73·53 | 74·0 | 73·4 | 72·06 | 69·2 | 68·9 | 68·41 |
| $LO, SO^3$ .... | 54·4 | 100·00 | 100·0 | 100·0 | 100·00 | 100·0 | 100·0 | 100·00 |

Crystallizes in combination with water, in shining rhombic prisms with dihedral summits (*Fig.* 93) (Hermann), and in long tables which effloresce very slightly in the air (C. Gmelin): the crystals decrepitate when heated, and give off their water of crystallization without first dissolving in it. They are very soluble in water (Arfvedson), but not perceptibly more so in hot water than in cold (Hermann); they are also easily dissolved by alcohol. (Kastner, *Kastn. Arch.* 16, 322.)

| | Crystallized. | | Hagen. | Arfvedson. | C. Gmelin. | Hermann. | Vauquelin. |
|---|---|---|---|---|---|---|---|
| LO..... | 14·4 | 22·71 | 22·61 | 26·87 | 27·25 | 85·7 | 87·5 |
| $SO^3$ ..... | 40·0 | 63·09 | 62·42 | 58·86 | 58·34 | | |
| HO ..... | 9·0 | 14·20 | 14·97 | 14·27 | 14·41 | 14·3 | 12·5 |
| $LO, SO^3 + Aq.$ | 63·4 | 100·00 | 100·00 | 100·00 | 100·00 | 100·0 | 100·0 |

*b. Acid salt.*—By evaporating *a* with sulphuric acid and heating to redness, a more fusible salt is obtained (Arfvedson), from which, when strongly ignited, the excess of acid is expelled in the form of sulphureous acid and oxygen gas. (C. Gmelin.) From its solution in water, however, the salt *a* separates in remarkably fine crystals, which have an acid reaction proceeding only from the adhering mother-liquor. (Arfvedson.)

G. SULPHIDE OF CARBON AND LITHIUM, and HYDROSULPHO-CARBONATE OF LITHIA.—The orange-yellow solution, when dried, yields a saline mass, which becomes moist in the air, even more readily than the potash or soda salt, and dissolves easily both in water and in alcohol. (Berzelius.)

### Lithium and Selenium.

Selenite of Lithia.—Fuses below redness, forming a yellow liquid, which solidifies on cooling to a clear pearly mass, having a broadly foliated crystalline texture; becomes moist in the air. (Berzelius, *Lehrb.* 4, 194.)

### Lithium and Iodine.

¶ A. Iodide of Lithium.—LiI + 6HO.—Forms acicular crystals, generally of a yellow colour, arising from the presence of free iodine; deliquescent; containing 28·30 per cent. of water. (Rammelsberg, *Pogg.* 66, 79.) ¶

B. Iodate of Lithia.—The aqueous solution when evaporated yields an anhydrous crust, soluble in 2 parts of cold, and not much less of hot water. (Rammelsberg, *Pogg.* 44, 555.)

¶ C. Periodate of Lithia.—Dissolves with tolerable facility in water, and is decomposed by alcohol. (Rammelsberg.) ¶

### Lithium and Bromine.

Bromate of Lithia.—The aqueous solution, evaporated in the usual way over oil of vitriol to a syrupy consistence, yields needles, which effloresce if kept long in the apparatus, but deliquesce rapidly in the open air. (Rammelsberg, *Pogg.* 55, 63.)

### Lithium and Chlorine.

A. Chloride of Lithium.—Crystallizes, on evaporating the aqueous solution in the sun, or an alcoholic solution over oil of vitriol (Rammelsberg), in cubes having the taste of common salt. (C. Gmelin.) When rapidly evaporated, it forms a crust. (Arfvedson.) Melts at a dull red heat, and volatilizes at a white heat. (C. Gmelin.) More volatile than chloride of potassium, but less volatile than chloride of sodium. (H. Rose.) In open vessels it volatilizes even at a low red heat, losing a portion of its chlorine and being partly converted into carbonate of lithia. (Hermann, H. Rose.)

*Tetra-hydrated chloride of lithium*, or *ter-hydrated hydrochlorate of lithia*.—Chloride of lithium, when it deliquesces in the air, gradually forms large rectangular prisms with four-sided summits placed upon the lateral edges (probably isomorphous with hydrated chloride of sodium &c.). When crystallized rapidly, it forms needles united together in feathery tufts, just like those of sal-ammoniac. When heated, the crystals undergo the aqueous fusion and afterwards dry up. Thrown on paper or moved with the fingers, they instantly become opaque, the opacity commencing at the point of contact and extending through the whole mass; in this state they fall to pieces on the slightest blow, and form a crystalline powder. (Hermann.)

Both the anhydrous and the hydrated chloride of lithium deliquesce very rapidly in the air, and are very soluble in water and in alcohol, (even absolute): the alcohol then burns with a red flame. (C. Gmelin.)

| | Anhydrous. | | Arfvedson. | | Hydrated. | | Hermann. |
|---|---|---|---|---|---|---|---|
| L | 6·4 | 15·31 | 22·39 | LCl | 41·8 | 53·73 | 53·64 |
| Cl | 35·4 | 84·69 | 77·61 | 4HO | 36·0 | 46·27 | 46·36 |
| LCl | 41·8 | 100·00 | 100·00 | LCl, 4Aq. | 77·8 | 100·00 | 100·00 |

¶ According to Rammelsberg (*Pogg.* 66, 79), the crystals contain only 2 atoms of water.

B. Chlorate of Lithia.—$LiO, ClO^5 + HO$.—Forms a radiated mass, very deliquescent, fusing at 50°, and evolving water at 140°, together with oxygen and small quantities of chlorine. After decomposition, chloride of lithium remains, having an alkaline reaction. The salt is very soluble in alcohol. (Wächter, *J. für pract. Chem.* 3, 321; *Ann. Pharm.* 52, 231.) ¶

C. Perchlorate of Lithia.—Carbonate of lithia is dissolved in the aqueous acid; the liquid evaporated to dryness; the residue dissolved in alcohol, which leaves behind any potash-salt that may be present; and the filtrate left to evaporate in a hot air chamber. Long, transparent, deliquescent needles (Serullas.)

## Lithium and Fluorine.

A. Fluoride of Lithium.—Crystallizes on evaporating the aqueous solution in very small opaque crystalline grains, which, at the temperature of commencing redness, fuse to a clear mass, which again becomes cloudy as it solidifies. Scarcely soluble in water. (Berzelius, *Pogg.* 1, 17.)

B. Fluoride of Lithium and Hydrogen.—Small crystals, having a very acid taste. Leaves fluoride of lithium when ignited. Difficultly soluble in water, but more soluble than the fluoride of lithium. (Berzelius.)

C. Fluoride of Lithium and Boron.—Prepared by precipitating the compound of hydrofluoric acid with borate of baryta by sulphate of lithia. Crystallizes, when slowly evaporated at a temperature of 40°, in large prisms. Tastes like the soda-salt. In the air it becomes moist and liquefies; and the liquid yields small, rhombohedral, very soluble crystals, which have not been further examined. Easily soluble in water. (Berzelius.)

## Lithium and Nitrogen.

A. Nitrate of Lithia.—Anhydrous rhombic prisms (C. Gmelin), which fuse to a clear liquid when gently heated. The salt tastes like nitre (Arfvedson); has a very acrid taste. (Vauquelin, C. Gmelin.) Deliquesces with great rapidity in the air; very soluble in strong alcohol. (C. Gmelin.)

B. Phosphate of Lithia and Ammonia.—Falls down in transparent crystalline grains during the slow evaporation of an aqueous solution of a salt of lithia mixed with phosphate of ammonia. It is not formed, if excess of phosphoric acid is present, or if the solution is very dilute; for then the ammonia escapes during the evaporation. It resembles in appearance the phosphate of magnesia and ammonia, and readily fuses in the blowpipe flame, with loss of ammonia; it then gives a blue colour with nitrate of cobalt. (Berzelius, *Lehrb.* 4, 213.)

C. Sulphate of Lithia and Ammonia.—This salt crystallizes in a table form, dissolves easily in water, and when heated to redness, leaves simple sulphate of lithia. (Arfvedson.)

## Lithium and Sodium.

Phosphate of Lithia and Soda.—Formed when the solution of a salt of lithia is evaporated to dryness with phosphate of soda. The liquid becomes turbid on evaporation, but the greater part of the double salt appears not to be formed till the liquid is evaporated to dryness: it is then left undissolved on treating the residue with water. If a salt of lithia is evaporated with metaphosphate or pyrophosphate of soda, the liquid is, in the first case, rendered still more turbid; but after complete evaporation, the same quantity of the same salt is formed in both cases. White bulky powder, fusing with tolerable facility on platinum wire before the blowpipe, and forming a clear bead, which, on cooling, becomes white, opaque, and crystalline; when fused on charcoal, it behaves in the same manner. Caustic lime or carbonate of lime decomposes it at a red heat. If the salt is heated to redness with 3 parts of hydrate of lime, boiling water will extract the lithia; and by evaporating, filtering from carbonate of lime, saturating the filtrate with hydrochloric acid, evaporating to dryness, and exhausting the residue with alcohol, it may be obtained in the form of chloride of lithium. When fused with carbonate of soda, with which it forms a clear glass, becoming turbid as it cools, it does not attack the platinum vessel; but when it is fused with carbonate of lime, then moistened with water, and heated again, the platinum is attacked. It is scarcely soluble in cold water, but somewhat more so in hot: in water containing phosphate of soda it is nearly insoluble. (Berzelius, *Schw.* 44, 127; *Pogg.* 4, 246; *Lehrb.* 4, 192.) It dissolves in 1400 parts of water at 15°; in 1233 at 60°; and in 951 parts at 100°. (Brandes, *Schw.* 59, 359.)

| | Fused, according to Berzelius. | | |
|---|---|---|---|
| NaO | 31·2 | | 26·66 |
| LO | 14·4 | | 12·31 |
| $PO^5$ | 71·4 | | 61·03 |
| NaO, LO, $PO^5$ | 117·0 | | 100·00 |

¶ Rammelsberg (*Pogg* 66, 79) finds that the composition of this salt varies very considerably, the quantity of lithia varying within the limits of 21·8 and 32·15 per cent.; from which he concludes that the two bases are capable of replacing each other in the salt. Moreover, he is of opinion that it is tribasic; because, when dissolved in dilute nitric acid, it gives a pure yellow precipitate with nitrate of silver. ¶

Lithia also combines with mercury.

## Chapter IV.

# BARIUM.

*History.* The earlier chemists distinguished lime and magnesia, under the appellation of *terræ absorbentes*, from the *Earths in a more limited sense:* to these *absorbent* or *alkaline* earths, baryta, discovered in 1774 by Scheele (*Opusc.* 2, 262), and strontia, discovered still later, were afterwards added. Since the time of Fourcroy, however, these earths, sometimes with the exception of magnesia, have been more or less regarded as alkalis; inasmuch as they possess the most characteristic properties of alkalis, and are distinguished from those earlier discovered, only by being —together with their compounds with acids—less easily soluble in water. They may therefore be distinguished as the *less soluble* or *earthy alkalis.* Sir H. Davy, in 1808, first obtained barium, strontium, and calcium in the free state; but they had before been obtained in combination with mercury, by Berzelius & Pontin.

*Sources.* As sulphate and carbonate of baryta; further, in Barytocalcite, in certain ores of manganese, in Harmotome and Brewsterite. Traces of baryta are also found in the water of Pyrmont (Brandes, *Schw.* 45, 369), of Kreuznach (Löwig), and of Luhatschivitz. (Planiava.)

*Preparation.*—1. Hydrate of baryta, or the carbonate, chloride or nitrate, is made into a doughy mass with water, formed into a cup, and placed upon a platinum dish, which is connected with the positive pole of a voltaic battery of 500 pairs of plates; the cup is filled with mercury, in which the negative wire dips (I., 458). The amalgam of barium thus obtained is heated in a tube of glass without lead, and filled with the vapour of rock-oil till all the mercury is sublimed. (H. Davy.) If the hydrate of baryta is mixed with oxide of mercury, the amalgam is obtained in larger quantity. (H. Davy.) Hare (*N. Bibl. Univ.* 23, 200; also *J. pr. Chem.* 19, 249) prepared the amalgam in a similar manner from moistened chloride of barium surrounded with a freezing mixture, using 2 batteries, each of 100 pairs, and containing more than 100 square feet of zinc. The mercury was expelled by heating the amalgam in an iron crucible provided with an iron cover, and exhausted of air.—2. According to Davy, barium may be obtained in an impure state, by passing vapour of potassium over red-hot baryta or chloride of barium.—3. Pure baryta or the nitrate is placed in a hole made in a piece of charcoal or on a slate, and exposed to a burning jet of detonating gas, produced from 3 measures of hydrogen and one measure of oxygen gas. Effervescence takes place, and white, shining globules of metallic barium are formed. The baryta must be anhydrous, and the detonating gas must be passed

through oil, not water; otherwise a translucent, vitreous, or horny mass will be obtained. (Clarke, *Gilb.* 62, 363; *Schw.* 18, 246; 21, 385; *Ann. Phil.* 17, 419.)

*Properties.* Silver-white, with less lustre than cast iron. Sinks rapidly in oil of vitriol, even if surrounded with bubbles of gas. Ductile, and may be beaten flat, though with difficulty. Fuses below redness, and does not volatilize at a red heat. (H. Davy, *Phil. Trans.* 1808, 343.) Of the colour and lustre of iron, and having a specific gravity = 4·0, or somewhat greater. (Clarke.)

*Atomic weight of Barium:* 68·39 (Berzelius); 68·64 (Pelouze); 68·54. (Marignac, *Ann. Pharm.* 68, 212.)

## *Compounds of Barium.*

### Barium and Oxygen.

### A. Baryta. BaO.

*Oxide of Barium, Heavy Earth, Schwererde, Schwerspatherde, Barytes, Terra ponderosa, Terre pesante, Terre barotique, Baryte, Protoxyde de baryum.*

*Formation.* Barium exposed to the air at ordinary temperatures becomes covered with a white crust of baryta, and crumbles to a white powder. (H. Davy, Clarke.) The oxidation is almost instantaneous, the metal becoming covered, first with a thin layer of a straw-yellow colour, and then with a thicker crust of oxide; so that to catch the real colour of the metal, the eye must follow the stroke of the file or the burnisher. (Hare.) Heated gently, it burns in the air with a dark-red light (H. Davy); in the flame of the oxy-hydrogen blowpipe, with a chrysolite-green light. (Clarke.) With water it forms baryta-water, with violent escape of hydrogen. (H. Davy, Clarke.) If the metal has been previously kept under rock-oil, the effervescence is slower, because the barium is covered with a layer of resin. (Hare.) In oil of vitriol it is converted, with evolution of hydrogen gas, into sulphate of baryta. (H.Davy.)

*Preparation.*—1. Nitrate of baryta is heated in a platinum or earthen crucible or in a porcelain retort, till it is completely decomposed,—a moderate heat being applied at first, and a very strong heat for a short time towards the end of the process. (Vauquelin.) The crucible is raised to a bright red heat in a good air-furnace—a few spoonfuls of powdered nitrate thrown in—the cover put on—and the whole exposed to a red heat till the mass has become quite solid; more nitrate is then added, and the process continued till the crucible is half full of baryta. If too much nitrate is added at once, the mass boils over. From a platinum crucible the baryta is not easily separated; and, according to Berzelius (*Lehrb.* 4, 243), a considerable quantity of oxide of platinum becomes mixed with the baryta. From an earthen crucible (which may be broken when cold) the baryta extracts silica, alumina, iron, and manganese. By too long an exposure to heat, the baryta absorbs carbonic acid and oxygen.—2. Carbonate of baryta mixed with $\frac{1}{10}$ *of its weight of lamp*-black or charcoal, and sometimes made into a thick

paste with solution of gum tragacanth or fixed oil, is heated to whiteness in an earthen crucible lined with lamp-black and having a closely fitting cover. (Pelletier.) When thus prepared, the baryta is often mixed with charcoal or carbonate of baryta: some cyanide of barium is also produced, unless the charcoal is perfectly free from nitrogen.—3. Carbonate of baryta is exposed in a platinum crucible to the strongest heat of a smith's forge till it fuses. (Abich.)

*Properties.* As prepared according to the first and second methods, it is a greyish-white, porous, friable mass; that obtained by the third method is dark grey with a bluish surface, and very dense; specific gravity = 4·000 (Fourcroy), = 4·7322 nearly (Karsten). Fuses only in the strongest heat of a forge (Abich): in the oxy-hydrogen blowpipe flame it fuses to a lead-coloured slag, which, when exposed to the air, becomes covered with a white powder. (Clarke.) It is a non-conductor of electricity. Has a caustic and alkaline taste, and acts as an alkali on vegetable colours. Corrodes organic matter, but less powerfully than potash or soda; it possesses poisonous properties independent of its causticity.

| | Calculation. | | Berzelius. | H. Davy. |
|---|---|---|---|---|
| Ba | 68·6 | 89·56 | 89·55 | 89·7 |
| O | 8·0 | 10·44 | 10·45 | 10·3 |
| BaO | 76·6 | 100·00 | 100·00 | 100·0 |

(BaO = 856·88 + 100 = 956·88. Berzelius.)

*Decompositions.*—1. By electricity.—2. By potassium at a red heat.—3. By hydrogen at the temperature of the oxy-hydrogen blowpipe.—4. By phosphorus, sulphur, and hydrogen acids.—5. When vapour of sulphide of carbon is passed over baryta heated in a tube, the baryta becomes red-hot, and is converted into a mixture of sulphide of barium and carbonate of baryta. (Berzelius.)

$$3BaO + CS^2 = 2BaS + BaO,CO^2.$$

*Combinations.* *a.* With water:

*a.* HYDRATE OF BARYTA.—When baryta is moistened with water, it falls to pieces and becomes very hot, the heat being often sufficient to raise the hydrate produced to a red heat, and then fuse it. (Döbereiner, *Schw.* 6, 367.) Baryta fused in a platinum crucible attracts water and carbonic acid from the air so greedily that it expands the crucible. (Abich.) The hydrate is obtained by melting the crystals of baryta in a silver crucible, and heating to redness.—White powder, or fused white mass, of crystalline texture; fuses at a low red heat and forms an oily liquid.

| | Calculation. | |
|---|---|---|
| BaO | 76·6 | 89·5 |
| HO | 9·0 | 10·5 |
| BaO, HO | 85·6 | 100·0 |

Loses none of its water by strong ignition unless carbonic acid enters to supply its place. (Bucholz & Gehlen, *N. Gehl.* 4, 258.) In the most powerful heat of a blast-furnace it loses weight. (Abich.) Heated on charcoal, it fuses with violent effervescence (proceeding from the decomposition of the water), and sinks into the charcoal, forming a hard mass. (Berzelius.)

*β.* Crystallized Baryta.—1. Baryta prepared by method 1, 2, or 3, is dissolved in hot water and left to crystallize. For this purpose, one part of nitrate of baryta may be mixed and heated to redness with from 1 to 2 parts of powdered heavy spar: the mass does not froth up, even when strongly heated. (Mohr, *Ann. Pharm.* 27, 27.)—Or one part of nitrate of baryta is heated to redness with from $\frac{1}{2}$ to $\frac{3}{4}$ pt. of iron filings until perfectly decomposed. (Artus, *J. pr. Chem.* 6, 172; Wittstein, *Repert.* 65, 359.)—2. The sulphide of barium obtained by heating to redness 4 parts of heavy spar with 1 part of charcoal, is dissolved in water, and boiled with 1 part of oxide of copper till the liquid becomes quite colourless, and, with an excess of acetic acid present, no longer precipitates a salt of lead; it is then filtered from the sulphide of copper, and left to crystallize. (Darcet; A. Vogel, *N. Tr.* 3, 2, 545.) The liquid contains a small quantity of oxide of copper in solution. (H. Rose, *Pogg.* 12, 78.)—3. Baryta is thrown down in crystals by adding potash to a cold aqueous solution of chloride of barium, nitrate, or acetate of baryta; the crystals are washed with ice-cold water or alcohol, till all the potash-salt is separated: they are then dissolved in hot water, and the solution is left to crystallize. (Anfrye & Darcet, *A. Gehl.* 3, 325; Kirchhoff, *A. Gehl.* 4, 658; Pessina, *Brugn. Giorn.* 17, 265.) Transparent, colourles, four-sided, or flattened six-sided prisms with four-sided summits. The crystals heated to 100° melt, lose water, and leave a white friable residue containing 20·07 per cent. (2 At.) of water. This, when heated to redness in a crucible, froths up violently, fuses, and leaves hydrate of baryta in a state of tranquil fusion. (Smith, *Phil. Mag. J.* 9, 87; also *Pogg.* 39, 196.) The loss which the crystals sustain by ignition amounts to 50 per cent. (Bucholz.) Specific gravity, = 2·188. (Filhol.)

| | Calculation. | | Smith. | R. Phillips. | Noad. | H. Rose. | Dalton. |
|---|---|---|---|---|---|---|---|
| BaO | 76·6 | 48·61 | 48·21 | 47·28 | 46·94 | 46·66 | 30 |
| 9HO | 81·0 | 51·39 | 51·79 | 52·72 | 53·06 | 53·34 | 70 |
| BaO, 9Aq. | 157·6 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100 |

H. Rose and Noad state the amount of water in the crystals, according to their own analyses, as equal to 10 atoms: if this be the case, it must amount to 54 per cent. Noad also found only 9 atoms of water in the crystals sent to him by Smith: it remains therefore to be decided whether the crystals containing the smaller quantity of water had lost any previous to the analysis; or, what is more probable, whether those which were richer in water did not contain some of the mother-liquid enclosed within them. ¶ Filhol (*J. Pharm. & Chim.* 3, 7, 271; *Ann. Pharm.* 56, 222), in a more recent examination of the hydrate, found only 8 atoms of water. ¶

*γ.* Baryta-Water.—Hydrate of baryta dissolves in 20 parts of cold, and in 2 parts of boiling water. (H. Davy.) One part of anhydrous baryta dissolves at 13° in 35, at 47° in 7·5, and at 70° in 5·6 parts of water. (Osann.) It forms a colourless solution, which is not precipitated by alcohol, and when exposed to the air becomes covered with successive films of carbonate of baryta, till at last nothing remains but pure water.

*b.* With acids it forms the Baryta-salts. For many acids, the affinity of baryta is greater than that of any other salifiable base. For the preparation of the other salts of baryta, the very abundant substance, *Heavy-*

*spar*, is generally used; more rarely, *Witherite*. Heavy spar is converted by ignition with charcoal, into sulphide of barium, which, after being dissolved and filtered, is decomposed by the particular acid which will form the required salt.—Of all the alkaline salts, those of baryta are specifically the heaviest. They are colourless when the acid itself is colourless. Those which are soluble exhibit poisonous properties. Many baryta-salts impart a green colour to the flame of alcohol. Most of them are nearly or quite insoluble in water; but all, the sulphate only excepted, dissolve in dilute hydrochloric or nitric acid. Salts of baryta which contain no metallic acid, form, when fused with carbonate of soda on a platinum wire in the outer blowpipe flame, a transparent bead which becomes cloudy on cooling. This mixture when fused on charcoal, sinks into it. (This character distinguishes baryta from lime, and from the earths which do not dissolve in carbonate of soda and remain on the surface of the charcoal.) (Plattner, *J. pr. Chem.* 16, 467.) Baryta-salts dissolved in water or nitric acid produce, even when very dilute, a finely divided, white, pulverulent precipitate with sulphuric acid and its salts. If the solution is very dilute, or the acid in large excess, the precipitate does not appear for some time: it is insoluble in hydrochloric or nitric acid. An aqueous solution of sulphate of lime also precipitates the salts of baryta. A solution of nitrate of baryta containing only 1 part of baryta in 25,000 parts of water, gives a very distinct cloudiness with sulphuric acid or sulphate of soda; with 50,000 to 100,000 parts of water, it is rendered slightly turbid; with 200,000 to 400,000 parts, not till after some minutes; and with 800,000 parts, the reaction ceases altogether. (Lassaigne, *J. Chim. Med.* 8, 526.) A solution of chloride of barium containing 1 part of baryta in 71,000 parts of water, becomes turbid with sulphate of soda, after the lapse of half an hour. (Harting, *J. pr. Chem.* 22, 50.) Hydrofluosilicic acid gives with baryta-salts, after a while, a crystalline precipitate nearly insoluble in hydrochloric and nitric acid. One part of chloride of barium dissolved in 3,800 parts of water, still gives a precipitate with this acid. (Harting.) Monocarbonate of ammonia, potash, or soda, precipitates a salt of baryta from an aqueous solution in white flakes, soluble with effervescence in hydrochloric or nitric acid. Bicarbonate of potash precipitates a somewhat concentrated, but not a very dilute solution, unless with the aid of heat. Borax gives a white flaky precipitate at a certain degree of concentration only; but diphosphate or arseniate of soda gives a precipitate with a more dilute solution: this precipitate is easily soluble in hydrochloric or nitric acid. Monophosphate of soda ($NaO, 2HO, cPO^5$) does not give any precipitate. Iodate of soda precipitates the baryta completely as iodate, in the form of a white granular powder easily soluble in hydrochloric acid. Salts of baryta are precipitated yellow by chromate of potash, and perfectly, even when the solution is largely diluted. Simple oxalate or tartrate of ammonia, potash, or soda, gives a white precipitate, soluble in dilute hydrochloric acid. Free oxalic acid and binoxalate of potash produce, after some time and only from a concentrated solution, a crystalline precipitate of binoxalate of baryta. Alkaline succinates precipitate a concentrated solution immediately; a dilute solution, after some time only. Ferrocyanide of potassium gives a yellowish-white precipitate, provided the solution is not too dilute. Perchloric acid and sulphide of ammonium do not affect baryta-salts.

*c.* Baryta likewise combines with some of the earths and metallic oxides.—*d.* With certain substances of the organic kingdom.

### B. Peroxide of Barium. $BaO^2$.

Baryta heated to low redness in a glass or porcelain tube, rapidly absorbs oxygen passed over it (Gay-Lussac & Thénard); and indeed, as Thénard (*Ann. Chim. Phys.* 8, 308) supposed and Rammelsberg (*Pogg.* 44, 588) confirmed, one atom of baryta absorbs one atom of oxygen. *Preparation.*—1. By Thénard's method (II., 7).—2. Chlorate of potash is sprinkled in small quantities at a time on baryta at a low red heat. The baryta becomes red-hot. The mass when cold may be freed from the chloride of potassium mixed with it, by washing with cold water; the residue is hydrated peroxide of barium, which may be dried in the air at ordinary temperatures. (Liebig & Wöhler, *Pogg.* 26, 172.) Quesneville (*Ann. Chim. Phys.* 36, 108; also *Pogg.* 10, 620) heats nitrate of baryta in a porcelain retort furnished with a Welter's safety tube, till it evolves no more hyponitric acid but only pure oxygen; the residue is peroxide of barium free from nitric acid.

This process might give nitrite of baryta.

| | Calculation. | | |
|---|---|---|---|
| Ba | 68·6 | | 81·09 |
| 2O | 16·0 | | 18·91 |
| $BaO^2$ | 84·6 | | 100·00 |

Peroxide of barium is of a dark grey colour, and somewhat more fusible than the protoxide. (Gay Lussac & Thénard.) When very strongly heated, it evolves oxygen and is converted into baryta: in warm water it is resolved into oxygen gas and baryta-water; with carbonic acid gas it yields oxygen and carbonate of baryta; heated with hydrogen gas it emits sparks, and is converted into hydrate of baryta. Gives up its excess of oxygen to carbon, boron, phosphorus, sulphur, and the metals, at elevated temperatures, and to hydrosulphuric acid in the cold. (Gay-Lussac & Thénard.) Dissolves in hydrated acids, forming a salt of baryta, whilst its excess of oxygen passes over to a portion of the water, forming peroxide of hydrogen. When peroxide of barium is thrown into water, it diffuses itself through the liquid without rise of temperature, and produces *Hydrated Peroxide of Barium* in the form of a white powder. The same compound is precipitated in pearly scales when an excess of baryta-water is added to pure peroxide of hydrogen, or the hydrochlorate or nitrate of that compound; these scales are decomposed by water at 100° into oxygen gas and baryta-water, and are only slightly soluble in colder water. (Thénard, *Ann. Chim. Phys.* 8, 312.) The hydrate appears to contain 6 atoms of water. (Liebig & Wöhler.)

## Barium and Carbon.

A. Carbonate of Baryta.—*a. Monocarbonate.* Found native as Witherite. It is rapidly formed by exposing baryta, or the hydrate, crystals, or solution of baryta to the air.

*Preparation.*—1. An aqueous solution of chloride of barium or nitrate of baryta is precipitated by carbonate of ammonia and washed.—2. *An aqueous solution of* sulphide of barium [illegible] with carbonate of

soda free from sulphate, and the precipitate washed. This precipitate is more likely to be contaminated either with a sulphur compound, or—if carbonate of potash is used instead of carbonate of soda—with silica.—3. A crucible is filled with a mixture of 10 parts of heavy spar, 2 parts of charcoal, and 5 parts of pearlash; exposed to a full red-heat for several hours, till the mass fuses together; then taken out, and the crucible refilled, &c. The broken mass freed by washing with water from sulphide of potassium, leaves impure carbonate of baryta. This serves for the preparation of other baryta-salts by dissolving it in the various acids (they will however contain iron). (Anthon, *Repert.* 59, 326; *vid.* also Otto, *Ann. Pharm.* 26, 92.) In order to obtain the carbonate in crystals, a bag containing crystallized baryta is suspended in a mixture of baryta-water and solution of potash, and the air allowed to act on it. (Zoega, *Kastn. Arch.* 2, 17.)

The crystalline system of Witherite is the rhombohedral; primary form, a slightly obtuse rhomb. (Fig. 141, 137, 138 and others) $r^5 : r^5 = 91° 54'$; $r^1 : r^3 = 88° 6'$; $r : \sigma = 143° 23'$ and so on. (Hauy.) Sp. gr. = 4·301 (Mohr) = 4·3019. (Karsten.) The artificially prepared carbonate is generally in the form of a soft white powder. Fuses in a powerful blast-furnace (Abich), and in the flame of the oxy-hydrogen blowpipe. (Pfaff.) In fine powder it turns reddened litmus blue, and the colour of violets green. (Pleischl.)—Tasteless and poisonous.

| | Calculation. | | Schaffgotsch. | Berzelius. | Kirw., Pellet., Klapr., Clem., Desorm., Bérard. | Bucholz. |
|---|---|---|---|---|---|---|
| BaO | 76·6 | 77·69 | 77·63 | 77·9 | 78 | 79·94 |
| $CO^2$ | 22·0 | 22·31 | 22·37 | 22·1 | 22 | 20·06 |
| BaO, $CO^2$ | 98·6 | 100·00 | 100·00 | 100·0 | 100 | 100·00 |

| | Withering. | Berthollet. | Fourcroy. |
|---|---|---|---|
| BaO | 78·6 | 79 | 90 |
| $CO^2$ | 21·4 | 21 | 10 |
| | 100·0 | 100 | 100 |

On charcoal ignited in a stream of oxygen gas, it volatilizes with a yellowish light. When exposed for an hour and a half to the strongest heat of a blast-furnace, it loses all its carbonic acid. (Abich, *Pogg.* 23, 314.) This occurs at a lower temperature, if vapour of water is passed over it, whereby the hydrate is formed. (Priestley, Gay-Lussac & Thénard, *Recherch.* 2, 180.) Fuses readily before the blowpipe, forming a clear bead (of hydrate?), which becomes white and opaque as it cools; on charcoal it behaves just like the hydrate. (Berzelius.) When carbonate of baryta is mixed under water with its own weight of sulphate of potash or twice its weight of Glauber's salts, and agitated, the whole is converted, in the course of half an hour, into sulphate of baryta and carbonate of potash or soda (*Sch.* 93); but at a higher temperature, the reverse takes place. (Kölreuter, *Mag. Pharm.*, 8, 181.) The decomposition of sulphate of potash or soda in the cold takes place, but very imperfectly, even when equal weights are used and the mixture agitated for 24 hours. (Gossmann, *Repert.* 61, 49.) Carbonate of baryta dissolves very easily in a cold aqueous solution of chloride of ammonium, or of nitrate or succinate of ammonia. (*A. Vogel, J. pr. Chem.* 7, 453; Brett, *Phil. Mag. J.* 10, 96;

Wittstein, *Repert.* 57, 18; Wackenroder, *Ann. Pharm.* 41, 315.) If the liquid be continuously boiled, one atom of sal-ammoniac only is required for the solution of one atom of carbonate of baryta, and the ammonia escapes as carbonate. (D. Smith, *Phil. Mag. J.* 9, 540; Demarçay, *Ann. Pharm.* 11, 251.) Carbonate of baryta is soluble in 4304 parts of cold, and in 2304 parts of boiling-water. (Fourcroy, *Ann. Chim.* 4, 64.) ¶ One part of carbonate of baryta dissolves in 14,137 parts of water at a temperature between 16° and 20°; in 15,421 parts of boiling water; and in 141,000 parts of solution of ammonia or carbonate of ammonia, at ordinary temperatures. (Fresenius, *Ann. Pharm.* 59, 117.) ¶ The aqueous solution has a slight alkaline reaction on vegetable colours. (Braconnot, Pleischl.) It does not dissolve in an aqueous solution of potash or soda salts.

*b. Sesquicarbonate.*—Chloride of barium is precipitated in the cold with sesqui-carbonate of potash dissolved in water. It is more soluble in water than *a*. (Boussingault, *Ann. Chim. Phys.* 28, 288.)

| | Calculation. | | Boussingault. |
|---|---|---|---|
| $2BaO$ | 153·2 | 69·89 | 68·5 |
| $3CO^2$ | 66·0 | 30·11 | 31·5 |
| $2BaO, 3CO^2$ | 219·2 | 100·00 | 100·0 |

*c. Bicarbonate.*—Can be prepared only in the form of aqueous solution.—1. Solution of carbonic acid dissolves $\frac{1}{830}$ of carbonate of baryta. (Fourcroy.)—2. By mixing a soluble salt of baryta with bicarbonate of potash or soda, acid carbonate of baryta is obtained and remains dissolved if a large quantity of water is used. (Berthollet, *N. Gehl.* 3, 261; Longchamp, *Ann. Chim. Phys.* 23, 191.) The solution has an alkaline action on litmus and violets. (Pleischl.)

## Barium and Boron.

Borate of Baryta.—*a. Monoborate.* Formed when chloride of barium is precipitated by monoborate of potash. The precipitate dissolves slightly in cold water, and more freely in hot. (Berzelius.)

*b. Biborate.*—By precipitating solution of borax with a baryta-salt in excess, and washing the precipitate. It forms loose hydrated flakes, which form a fine white powder when dried, and when heated to redness, give off water and fuse to a grey transparent glass. Exerts a slight alkaline action on vegetable colours.

| | Fused. | | Tünnermann. | L. Gmelin. | Berzelius. | Thénard. |
|---|---|---|---|---|---|---|
| $BaO$ | 76·6 | 52·39 | 52·79 | 54·9 | 55·8 | 57·8 |
| $2BO^3$ | 69·6 | 47·61 | 47·21 | 45·1 | 44·2 | 42·2 |
| $BaO, 2BO^3$ | 146·2 | 100·00 | 100·00 | 100·0 | 100·0 | 100·0 |

| | Unignited. | | Tünnermann. |
|---|---|---|---|
| $BaO$ | 76·6 | 46·65 | 46·71 |
| $2BO^3$ | 69·6 | 42·39 | 41·79 |
| $2HO$ | 18·0 | 10·96 | 11·50 |
| $BaO, 2BO^3 + 2Aq.$ | 164·2 | 100·00 | 100·00 |

When chloride of barium is precipitated by borax in excess, the precipitate after ignition contains 48·31 per cent. of baryta and 51·79 of boracic

acid.](Tünnermann.) With sulphate of potash and soda in the cold, it behaves in the same manner as carbonate of baryta. (Kölreuter.) It dissolves in 100 parts of cold water: a hot saturated solution deposits part of the salt on cooling, in the form of a white powder; carbonic acid, according to Berzelius, throws down carbonate of baryta from the solution. It is readily dissolved by a cold aqueous solution of chloride of ammonium or nitrate of ammonia, (Brett, Wackenroder,) also by chloride of barium. (H. Rose.)

*c. Sexborate.*—Sexborate of ammonia gives with baryta-salts a white precipitate, which is soluble in a large quantity of water, and renders it alkaline. (Laurent.)

## Barium and Phosphorus.

A. Phosphide of Barium. Otherwise called *phosphuret of baryta*.—It is obtained, mixed with phosphate of baryta, when vapour of phosphorus is passed over baryta heated to redness in a glass tube. Dry phosphorus is put into a glass tube from $\frac{1}{4}$ inch to $\frac{1}{2}$ inch wide, sealed at one end, the rest of the tube, excepting the length of 2 inches beyond the phosphorus, being filled with pieces of baryta. The tube is placed horizontally; the part containing the baryta heated to low redness by means of charcoal; and the phosphorus gently fused and volatilized by a charcoal fire or a spirit lamp. If all the air is previously expelled from the tube by a current of hydrogen gas, and the vapour of phosphorus mixed with hydrogen passed over the baryta, 74·04 parts of baryta absorb 25·96 parts of phosphorus, or 7 atoms of baryta take up 6 atoms of phosphorus. In this manner, 5 atoms of monophosphide of barium and 1 atom of diphosphate of baryta are produced.

$$7BaO + 6P = 5BaP + 2BaO, PO^5.$$

(Dumas, *Ann. Chim. Phys.* 32, 364.) [Should not $3BaO, PO^5$ be formed, according to the formula $8BaO + 6P = 5BaP + 3BaO, PO^5$?] This substance is brownish-black, has a metallic lustre, and is tolerably hard. (Dumas.) Very fusible. Decomposed by water into phosphuretted hydrogen gas and hypophosphite of baryta. (Dulong.) Not sensibly affected by chlorine in the cold; but when heat is applied, it immediately becomes red-hot and is resolved into chloride of phosphorus, chloride of barium, and phosphate of baryta. (Dumas.)

B. Hypophosphite of Baryta.—1. Phosphide of barium is decomposed by water, the liquid filtered, and evaporated to the crystallizing point. (Dulong.)—2. Baryta-water is boiled with phosphorus till no more phosphuretted hydrogen is evolved; the solution filtered from the phosphate of baryta produced at the same time; then evaporated over oil of vitriol in vacuo, and the uncrystallizable residue dissolved in hot water and cooled. (H. Rose.) As it is not absolutely necessary to boil the baryta-water with the phosphorus, the flask may be nearly filled with liquid and set in a warm place; and thus the explosion which the phosphuretted hydrogen produces on coming in contact with the air may be prevented. (Wurtz.) [A cast-iron bottle might be serviceable.] Instead of baryta-water, a solution of ordinary sulphide of barium, which generally contains more than one atom of sulphur, may be used: it acts in the cold, and loses

its yellow colour, while the phosphorus absorbs the excess of sulphur, and is resolved, together with the water, into hydrosulphuric acid which combines with the monosulphide of barium, and hypophosphorous acid. If heat be applied, a violent evolution of easily inflammable phosphuretted hydrogen and pure hydrogen gas, followed by a small quantity of hydrosulphuric acid gas, takes place. At last a solution is obtained, consisting of hypophosphite of baryta and double sulphide of hydrogen and barium, which latter is not decomposed by phosphorus. The double sulphide is decomposed by digestion with carbonate of lead; and the liquid filtered and evaporated to the crystallizing point, yields the salt *b*. (Wurtz.)

*a. With 2 atoms of water.*—1. Crystallizes from a solution evaporated in vacuo over oil of vitriol already mixed with water (H. Rose); likewise from a solution in excess of hypophosphorous acid: none of that acid combines with the crystals, so that they are neutral after washing. (Wurtz.)—2. It remains after drying the salt *b* at 100°. (Wurtz.) Prepared by the first method, it forms shining square tables. (Wurtz.)

*b. With 3 atoms of water.*—Crystallizes from a hot aqueous solution on cooling (H. Rose), or on the careful addition of alcohol, till turbidity begins to show itself and the deposition of salt commences. (Wurtz.) Crystallizes in prisms of a pearly lustre and somewhat flexible. (H. Rose.) White needles, permanent in the air when dry, and losing 6·28 per cent. of water at 100°. When heated, the salt first evolves water, then a large quantity of spontaneously inflammable phosphuretted hydrogen, followed by a little non-spontaneously inflammable gas, and leaves 80·74 per cent. of a reddish mixture of diphosphate of baryta with a small quantity of oxide of phosphorus. (H. Rose.)

$$2(BaO, 2HO, PO) = 2BaO, PO^5 + PH^3 + HO.$$

A concentrated solution heated with hydrate of potash evolves much hydrogen and deposits phosphite of baryta. (Wurtz.)

$$2(BaO, 2HO, PO) + 2KO = 2BaO, PO^3 + 2KO, PO^3 + 4H.$$

The salt *b* dissolves in 3·5 parts of cold and in 3 parts of boiling water (Wurtz); it is insoluble in alcohol. (H. Rose.) (*Vid.* also Dulong, *Ann. Chim. Phys.* 2, 141; H. Rose, *Pogg.* 9, 370, 12, 83; Wurtz, *Ann. Pharm.* 43, 323.)

| | With 2 atoms of water. | | | H. Rose. *a.* |
|---|---|---|---|---|
| BaO | 76·6 | 57·16 | | 85·57 |
| PO | 39·4 | 29·40 | | |
| 2HO | 18·0 | 13·44 | | 14·43 |
| BaO, 2HO, PO | 134·0 | 100·00 | | 100·00 |

| | | Wurtz. | H. Rose. |
|---|---|---|---|
| *a.* | With 3 atoms of water. | *β.* | *γ.* |
| BaO | 76·6 | 53·44 | 52·16 |
| PO | 39·4 | 27·46 | |
| 3HO | 27·0 | 19·10 | 21·01 |
| + Aq. | 143·0 | 100·00 | 100·00 |

*α* consists of crystals obtained by evaporating the solution in vacuo over oil of vitriol containing water; *β*, of crystals formed by the cooling

of an aqueous solution; $\gamma$ is the dry mass which remains in vacuo over pure oil of vitriol.

C. PHOSPHITE OF BARYTA.—a. *Diphosphite.* Precipitates on mixing diphosphite of ammonia with chloride of barium: it separates after a short time as a white crystalline crust, which adheres to the vessel and effloresces in dry air. (Berzelius.) The dry salt heated to redness in a retort evolves pure hydrogen gas, besides traces of water and phosphorus, and leaves di-[pyro-]phosphate of baryta, of a brownish colour, arising from the presence of a small quantity of phosphoric oxide.

$$2BaO, PO^2, 2HO = 2BaO\ PO^5 + 2H.$$

(H. Rose, *Pogg.* 9, 23.) Evaporated with nitric acid and ignited, it leaves diphosphate of baryta. (Berzelius.) Dissolves readily in water containing sal-ammoniac. (Wackenroder.) Very slightly soluble in water, from which it crystallizes by evaporation: when strongly heated with water, it is converted into a basic salt which separates in pearly scales, and an acid salt which remains in solution. (Dulong.)

| | Calculation. | | Berzelius. | H. Rose. | Fourcroy & Vauquelin. |
|---|---|---|---|---|---|
| 2BaO | 153·2 | 67·61 | 67·24 | 66·65 | 51·3 |
| $PO^2$ | 55·4 | 24·45 | 24·31 | 25·30 | 41·7 |
| 2HO | 18·0 | 7·94 | 8·45 | 8·05 | 7·0 |
| $2BaO, PO^2, 2Aq.$ | 226·6 | 100·00 | 100·00 | 100·00 | 100·0 |

When a solution of monophosphate of baryta is precipitated by excess of ammonia, digested, filtered and washed (but not too long, on account of its solubility) a salt remains containing 69·47 per cent. (5 atoms) of baryta, 28·85 (3 atoms) of phosphorous acid, and 1·65 (2 atoms) of water. (H. Rose.)

*b. Monophosphite.*—The salt *a* is digested with an aqueous solution of phosphorous acid, in quantity not quite sufficient to form a perfect solution, and the filtrate evaporated in vacuo over oil of vitriol. It forms small granular crystals. Heated in a retort, it swells up considerably; evolves a mixture of hydrogen gas and much phosphuretted hydrogen, not spontaneously inflammable; and leaves a residue free from oxide of phosphorus, composed of 55·9 parts (10 atoms) of baryta and 46·1 parts (9 atoms) of phosphoric acid. Evaporated with nitric acid and ignited, it leaves 95·8 per cent. of fused monophosphate of baryta ($BaO, PO^5$). Easily soluble in water. (H. Rose, *Pogg.* 9, 215.)

| | Crystallized. | | H. Rose. |
|---|---|---|---|
| 2BaO | 153·2 | 49·42 | 49·59 |
| $2PO^3$ | 111·8 | 36·07 | 35·83 |
| 5HO | 45·0 | 14·51 | 14·58 |
| $2(BaO, 2HO, PO^5) + Aq.$ ? | 310·0 | 100·00 | 100·00 |

D. ORDINARY PHOSPHATE OF BARYTA.—*a. Triphosphate.* Formed when chloride of barium is precipitated by triphosphate of soda: the supernatant liquid is neutral. Heavy precipitate in the form of small flakes. (Graham, *Pogg.* 32, 49.)

| | Calculation. | |
|---|---|---|
| 3BaO | 229·8 | 76·29 |
| $cPO^5$ | 71·4 | 23·71 |
| $3BaO, cPO^5$ | 301·2 | 100·00 |

By digesting the salt *b* with ammonia, Berzelius (*Ann. Chim. Phys.* 21, 114) obtained a white powder which did not absorb carbonic acid from the air; it contained 72·93 per cent. of baryta with 27·07 of phosphoric acid. This is either, as Berzelius supposes, a compound of 5 atoms of baryta with 2 atoms of phosphoric acid, or a mixture of *a* and *b*.

*b. Diphosphate.*—1. Ordinary diphosphate of ammonia is added drop by drop to an aqueous solution of chloride of barium, in such quantity that the former salt may predominate. (Berzelius.) An excess of diphosphate of ammonia would withdraw one part of the acid from the precipitate, and become changed into simple phosphate of ammonia. (Mitscherlich.)—2. ¶ Ludwig (*Arch. d. Pharm.* 66, 265) found that on adding chloride of barium to ordinary phosphate of soda, the compound $2BaO, HO, PO^5$, is always precipitated, and more or less phosphoric acid left in solution: moreover, when phosphate of baryta is dissolved in hydrochloric acid and precipitated by ammonia, phosphoric acid is likewise found in the liquid. ¶ White pulverulent precipitate, fusing in the fire to a grey enamel. (Berzelius.) With a cold solution of potash or soda it behaves like carbonate of baryta. (Kölreuter.) This decomposition is very imperfect. (Gossmann.) Readily dissolved by aqueous phosphoric, hydrochloric, or nitric acid. It is easily soluble also in water containing sal-ammoniac, nitrate, or succinate of ammonia from which it is partially precipitated by a small quantity of ammonia, but completely by a larger quantity. (H. Rose, Brett, Wittstein.) Dissolves at 22·5°, in 400 parts of acetic acid of specific gravity 1·032. One part of it dissolves in 20,570 parts of water at 20°. (Bischof.) If an excess of phosphate of baryta is digested at a temperature of 20° in nitric acid of specific gravity 1·275 mixed with various proportions of water, the salt dissolves in the several liquids in very different proportions. In the following table, *a* gives the quantity of water added to 100 parts of nitric acid; *b*, how many parts of the acid mixture are required to dissolve 1 part of phosphate of baryta; *c*, the quantities of phosphate of baryta dissolved by 100 parts of nitric acid of specific gravity 1·275, after dilution with a greater or smaller quantity of water. (Bischof, *Schw.* 67, 39.)

| *a.* | *b.* | *c.* | *a.* | *b.* | *c.* | *a.* | *b.* | *c.* |
|---|---|---|---|---|---|---|---|---|
| ·0 | 1563 | 0·062 | 396 | 57 | 8·74 | 1000 | 22 | 49·91 |
| 79·2 | 318 | 0·56 | 475·2 | 45 | 12·88 | 1100 | 45 | 26·78 |
| 158·4 | 155 | 1·67 | 700 | 52 | 15·53 | 1700 | 66 | 27·30 |
| 237·5 | 107 | 3·16 | 800 | 48 | 18·65 | 2300 | 63 | 38·02 |
| 316·8 | 69 | 6·03 | 900 | 30 | 33·02 | 2900 | 74 | 39·16 |

Hence it appears that 100 parts of nitric acid of specific gravity 1·275 dissolve the greatest quantity of the salt when diluted with a tenfold quantity of water. [The solution is doubtless effected by the conversion of the diphosphate of baryta into nitrate and soluble monophosphate of baryta. The more concentrated the solution the less easily is the nitrate of baryta taken up. A certain degree of dilution is therefore necessary; but when it is too great, the decomposing effect of the nitric acid is probably interfered with.] Water containing $\frac{1}{10000}$ part of nitric acid dissolves more than double the quantity that pure water does. (Bischof.)

*c. Two-thirds phosphate.* When an aqueous solution of phosphoric acid is saturated with the salt *b*, and alcohol added, large flakes are thrown down, which, after being purified by means of alcohol and dried,

yield a loose white powder, and after ignition—during which the mass puffs up—a grey porous mass. (Berzelius.) [After ignition, it probably consists of pyrophosphate and metaphosphate of baryta.]

| | | Ignited. | |
|---|---|---|---|
| 3BaO | 229·8 | | 61·67 |
| $2PO^5$ | 142·8 | | 38·33 |
| $3BaO, 2PO^5$ | 372·6 | | 100·00 |

*d. Monophosphate.* Monophosphate of soda does not affect chloride of barium; the slightest addition of ammonia, however, gives rise to a precipitate. (Mitscherlich.)—Diphosphate of baryta is dissolved in aqueous phosphoric acid to saturation; the solution evaporated gradually; and the crystals formed during the process pressed between blotting-paper. The syrupy mother-liquid is phosphoric acid nearly free from baryta. The crystals are white, and resemble chloride of barium in taste as well as in appearance, excepting that they are rather acid and redden litmus. They are permanent in the air, and at a red heat are converted, with frothing up and loss of water, into a spongy mass resembling burnt alum. (Berzelius.) The salt dissolves in aqueous phosphoric acid and some other acids, without decomposition: mixed with a large quantity of water, it changes into diphosphate which remains undissolved, and dilute phosphoric acid containing but little baryta. (Berzelius, *Ann. Chim. Phys.* 2, 153; 11, 114.)

| | Ignited. | | Berzelius. |
|---|---|---|---|
| BaO | 76·6 | 51·76 | 52·2 |
| $PO^5$ | 71·4 | 48·24 | 47·8 |
| $BaO, PO^5$ | 148·0 | 100·00 | 100·0 |

| | Crystallized. | | Berzelius. |
|---|---|---|---|
| BaO | 76·6 | 46·15 | 46·46 |
| $cPO^5$ | 71·4 | 43·01 | 42·54 |
| 2HO | 18·0 | 10·84 | 11·00 |
| $BaO, 2HO, cPO^5$ | 166·0 | 100·00 | 100·00 |

E. Dipyrophosphate of Baryta.—An aqueous solution of dipyrophosphate of soda gives with chloride of barium a precipitate containing 67·33 parts of baryta and 32·67 parts of pyrophosphoric acid. (Hess, *Pogg.* 18, 71.) Pyrophosphate of baryta is insoluble in water containing sal-ammoniac. ¶ Amorphous white powder, somewhat soluble in water; soluble in nitric and in hydrochloric acid; insoluble in acetic acid and solution of pyrophosphate of soda; soluble in water containing sulphurous acid; also in a large excess of pyrophosphoric acid. The hydrated salt contains one atom of water. (Schwarzenberg.) ¶

F. Metaphosphate of Baryta.—Metaphosphate of soda—prepared by igniting the ordinary monophosphate of soda—is dissolved in a small quantity of water, precipitated with excess of chloride of barium, and the abundant gelatinous precipitate well washed and dried. The transparent brittle mass obtained in the first instance, evolves water at a red heat, and undergoes partial fusion. After ignition it is dissolved with difficulty by nitric acid, and is insoluble in hot water; but after being boiled in water for some hours, it begins to dissolve, and continues to do so with increasing facility—the solution containing ordinary monophosphate of baryta, and giving a yellow precipitate with solution of silver. (Graham, *Pogg.* 32, 68.) *Water holding* sal-ammoniac in solution does

not dissolve it. Maddrell prepared this salt by dissolving carbonate of baryta in dilute phosphoric acid, evaporating to dryness, and heating the residue to a temperature of 316°.

| | Ignited. | | Graham. | | Maddrell. |
|---|---|---|---|---|---|
| | | | *a.* | *b.* | |
| BaO | 76·6 | 51·76 | 52·04 | 53·62 | 51·70 |
| $aPO^5$ | 71·4 | 48·24 | 47·96 | 46·38 | 48·30 |
| BaO, $aPO^5$ | 148·0 | 100·00 | 100·00 | 100·00 | 100·00 |

The salt *a* examined by Graham was obtained by precipitating with a large excess of chloride of barium; the salt *b*, by using a smaller quantity of the chloride; in this case the liquid remained acid.

¶ The salt is obtained in oblique rhombic prisms containing 2 atoms of water, by adding a solution of 1 part of the soda-salt in 10 or 15 parts of water to a nearly saturated solution of 2 or 3 parts of chloride of barium—filtering from the precipitate formed at first—and allowing the clear liquid to stand quietly for some time. (Fleitmann & Henneberg, *Ann. Pharm.* 65, 304.) ¶

## Barium and Sulphur.

A. Monosulphide of Barium.—Formerly called *sulphuret of baryta*. 1. Sulphuretted hydrogen is passed over baryta heated in a tube as long as water is formed. (Berzelius.)—2. Powdered sulphate of baryta is easily reduced by hydrogen gas, at a red heat. (Pagenstecher, *N. Tr.* 3, 1, 291.)—3. Sulphate of baryta is heated to redness with charcoal.

$$BaO, SO^3 + 4C = BaS + 4CO.$$

Whether a bright or a low red heat is applied, the aqueous solution of the sulphide of barium exhibits a pale yellow colour, and gives with acids a slight precipitate of sulphur, about the same in quantity in both cases. (H. Rose, *Pogg.* 55, 537.) Most of the sulphate of baryta is reduced by this method to monosulphide of barium; but a small portion of polysulphide [ter ?] and caustic baryta is produced,

$$3(BaO, SO^3) - 10O = 2BaO + BaS^3.$$

*a*. 100 parts of sulphate of baryta exposed to a strong white heat in a charcoal crucible yield 72 parts of sulphide of barium. (Berthier, *Ann. Chim. Phys.* 22, 231.) – *b*. In order to obtain other baryta compounds from the native sulphate, it is exposed to a full red heat with about one-fourth its weight of charcoal. As the mixture does not fuse, the heavy-spar must be finely pulverized and thoroughly incorporated with the charcoal; an addition of resin, oil, starch, &c., which promotes the close contact of the atoms, is of service*.

*c*. The mixture is ignited in a covered crucible of clay, or better, of cast-iron. The heat is continued for several hours till carbonic oxide no longer escapes from the mass. In operating on large quantities a pottery or tile furnace may be used. Berzelius recommends a mixture of 8 parts of heavy-spar, 1 part of charcoal, 2 parts of resin, and 2 parts of rye-meal.

* A very good method is to heat the heavy-spar with one-third of its weight of bituminous coal.—[W.]

*β*. A mixture of 1 part of powdered heavy-spar and ¼ pt. of charcoal —or better, the soot from pit-coal—is formed into sticks by means of a paste made with ⅛ pt. of starch. When the sticks are dry, a furnace is filled a foot high with burning charcoal; the sticks placed on it together with fresh fuel; the whole covered with more burning charcoal; and, as soon as the furnace is thoroughly red hot, the fire is covered over with ashes and bricks, and the furnace closed. The sticks, when cold, are found to be converted into sulphide of barium. (Liebig, *Ann. Pharm.* 35, 115.) Otto (*Ann. Pharm.* 26, 92) surrounds the sticks with paper. A suitable furnace for the purpose is described by Anthon. (*J. pr. Chem.* 8, 406.)

*γ*. To fuse the mass, and thereby bring about a readier decomposition of the sulphate of baryta, a potash or soda compound may be added to the mixture of heavy-spar and charcoal, which is to be heated to redness in the crucible. This addition occasions no inconvenience, if the object in view is to precipitate carbonate of baryta from the sulphide by means of carbonate of soda; but if other salts of baryta are to be prepared by addition of hydrochloric acid, &c., repeated crystallizations are required to remove the potash or soda salt mixed with the solution. Bucholz (*A. Gehl.* 1, 310) ignites 4 parts of heavy-spar with ½ (or better, 1) part of charcoal, and 1 part of common salt. Duflos (*Br. Arch.* 36, 275) uses 12 parts of heavy-spar with 3 parts of dry sulphate of soda, and 2 (or better, 3) parts of charcoal. The sulphide of barium obtained by either of these methods is dissolved in boiling water and filtered from undecomposed heavy-spar, charcoal, sulphide of iron, and other impurities, before adding the acid to form any particular salt. When powdered sulphate of baryta free from iron is ignited with a small quantity of carbonaceous matter, the Bolognian phosphorus is obtained (I., 193): this substance may be regarded as a mixture of sulphide of barium and undecomposed sulphate of baryta.

Sulphide of barium prepared according to method 3, *a*, is white and grey in some places, cohering loosely, and of a crystalline granular form. (Berthier.) That obtained from heavy-spar, according to method 3, b, *α* and *β*, is yellowish, or flesh-coloured, probably from the presence of sulphide of iron.

| | | Calculation. | |
|---|---|---|---|
| Ba | 68·6 | | 81·09 |
| S | 16·0 | | 18·91 |
| Ba, S | 84·6 | | 100·00 |

The sulphide of barium obtained by the third method, *a*, is scarcely altered by roasting, and detonates imperfectly with chlorate of potash, but perfectly with nitre. (Berthier.) When vapour of water is passed over sulphide of barium at a red heat, hydrogen gas is evolved, and sulphate of baryta formed. (Regnault, *Ann. Chim. Phys.* 62, 386.) It evolves sulphuretted hydrogen abundantly when decomposed by hydrated acids, even by nitric acid or aqua regia. (Berthier.) When exposed to the air, it is decomposed by the action of water and carbonic acid, and gives off a uniform and continuous current of sulphuretted hydrogen. It might be useful, therefore, to strew this substance on the floor of the apartments of invalids to whom the inhalation of sulphuretted hydrogen is of service.

With water, monosulphide of barium forms baryta and double sulphide of hydrogen and barium:

$$2BaS + HO = BaO + BaS,HS;$$

or baryta and bihydrosulphate of baryta:

$$2BaS + 2HO = BaO + BaO,2HS.$$

This result is deduced from the following experiments of H. Rose (*Pogg.* 55, 415): If sulphide of barium, prepared from sulphate of baryta and excess of charcoal at a white heat, is treated nine times in succession with a quantity of cold water less than sufficient to dissolve the whole, the mass being digested for 24 hours each time in a close vessel, the first two solutions are pale yellow, and when treated with hydrochloric acid, evolve large quantities of hydrosulphuric acid, together with a precipitate of sulphur; they also evolve abundance of hydrosulphuric acid, when treated with sulphate of manganous oxide. They therefore contain double sulphide of hydrogen and barium (bihydrosulphate of baryta) together with a polysulphide of barium. The third quantity behaves as a solution of monosulphide of barium (simple hydrosulphate of baryta) containing a slight excess of hydrosulphuric acid. The fourth is of the same character, but contains a slight excess of baryta. This excess goes on continually increasing in the fifth, sixth, and seventh solutions; and the eighth and last behave like pure baryta-water. A solution of sulphide of barium in not too large a quantity of boiling water, kept for some years in a stoppered bottle, deposits, first crystals of baryta, then scales ($\alpha$) which are a mixture of crystallized baryta and hydrated monosulphide of barium; and afterwards double six-sided pyramids ($\beta$) containing the same ingredients, but much richer in sulphide of barium. The mother-liquor boiled down still further in a retort, evolves a continuous current of hydrosulphuric acid gas, and on cooling deposits hydrated sulphide of barium in the form of a white powder (*a*, *b*, *c*), while double sulphide of hydrogen and barium remains in solution. (H. Rose, *Pogg.* 55, 415.)

*Hydrated Monosulphide of Barium*, or *Mono-hydrosulphate of Baryta.*—White powder, becoming yellow spontaneously when kept in close vessels. When treated at once with a quantity of water sufficient to dissolve it perfectly, it yields a solution which does not evolve hydrosulphuric acid when mixed with sulphate of manganous oxide; but an insufficient quantity of water extracts double sulphide of hydrogen and barium and leaves baryta undissolved. (H. Rose.)

| | Calculation. | | H. Rose. | | |
|---|---|---|---|---|---|
| | | | *a.* | *b.* | *c.* |
| BaS | 84·6 | 61·04 | 56·99 | 53·72 | 51·99 |
| 6HO | 54·0 | 38·96 | 42·09 | 41·82 | 40·99 |
| BaO | | | 0·92 | 4·46 | 7·02 |
| BaS, 6HO | 138·6 | 100·00 | 100·00 | 100·00 | 100·00 |

The three specimens examined by H. Rose were mixed with different quantities of hydrated baryta.

*Mixtures of Hydrated Sulphide of Barium with Hydrated Baryta.*

$\alpha$. *Scaly crystals.* About: 4 (BaO, 10HO) + 3 (BaS, 6HO). When dissolved in hot water, they yield crystals of pure baryta on cooling.

$\beta$. *Double six-sided pyramids.* BaO, 10HO + 3 (BaS, 6HO). Large, transparent and colourless crystals, deeply truncated, so as to form six-sided tables. (*Fig.* 133, H. Rose.)

| | Calculation. | | H. Rose. |
|---|---|---|---|
| 4BaO | 306·4 | 28·31 | 26·36 |
| 3BaS | 253·8 | 23·46 | 22·79 |
| 58HO | 522·0 | 48·23 | 50·85 |
| *a.* | 1082·2 | 100·00 | 100·00 |

| | Calculation. | | H. Rose |
|---|---|---|---|
| BaO | 76·6 | 13·15 | 12·64 |
| 3BaS | 253·8 | 43·58 | 44·14 |
| 28HO | 252·0 | 43·27 | 43·22 |
| *β.* | 582·4 | 100·00 | 100·00 |

B. Hydrated Sulphide of Hydrogen and Barium, or Bihydrosulphate of Baryta. 1. Baryta-water or monosulphide of barium reduced to a paste with water and warmed, is saturated with hydrosulphuric acid. The solution evaporated out of contact of air, and cooled, yields crystals of baryta and yellow prisms. The remaining liquid is either evaporated in vacuo, whereby white opaque prisms are obtained; or it is mixed with alcohol; filtered from the hyposulphite of baryta and sulphur, produced by air contained in the alcohol; and cooled down to $-10°$: in this manner, colourless and transparent four-sided prisms are produced.—2. Also when baryta or any of its hydrated compounds is allowed to crystallize, together with sulphide of barium, from an aqueous solution of monosulphide of barium, by evaporation in a retort and cooling, and the residual liquid (which is of a yellowish colour, from the air not being perfectly excluded) further evaporated and cooled, a crystalline mass of double sulphide of hydrogen and barium is obtained. (H. Rose.) The crystals contain water, which they lose when heated, becoming white at the same time. When exposed to the air, they effloresce and turn white, while hyposulphite and sulphate of baryta are formed. In a retort, they lose their water of crystallization without fusing, and then evolve hydrosulphuric acid as the temperature approaches redness, leaving dark yellow monosulphide of barium, which becomes white as it cools. An aqueous solution precipitates chloride of manganese with evolution of hydrosulphuric acid gas. (Berzelius, *Pogg.* 6, 441.) The salt, when boiled, evolves hydrosulphuric acid. With iodine, it forms iodide of barium and free hydriodic acid, sulphur being set free. It is insoluble in alcohol. (H. Rose.)

C. Tersulphide of Barium.—If 8 parts of baryta are ignited with 6 parts of sulphur, 1·78 parts of sulphur are volatilized, and a baryta liver of sulphur remains, from which water dissolves sulphide of barium, leaving behind 2·8 parts of sulphate of baryta. (Vauquelin, *Ann. Chim. Phys.* 6, 10.) [8 : 6 — 1·78 = 76, 6 : 40·4; so that 1 atom of baryta is united with $2\frac{1}{2}$ atoms of sulphur, or 4 atoms of baryta with 10 atoms of sulphur.]

$$4BaO + 10S = 3BaS^3 + BaO,SO^3.$$

If moistened tersulphide of barium is heated, or vapour of water passed over the ignited compound, hydrosulphuric acid is obtained [and sulphate of baryta !]. (Gay-Lussac, *Ann. Chim. Phys.* 40, 304.)

D. *Hydrated Pentasulphide of Barium* or *Hydrosulphite of Baryta.*—Prepared by boiling an aqueous solution of sulphide of barium (or double sulphide of hydrogen and barium, which then evolves sulphuretted hydrogen; *H. Rose*) with sulphur. Also by boiling baryta-water with sulphur; but in this case hyposulphite of baryta is produced at the same time. (Berzelius.) It forms a yellow, bitter, alkaline and caustic liquid, which, when evaporated in vacuo, leaves a pale yellow amorphous mass, and is decomposed in the air, with deposition of sulphur and formation of hyposulphite of baryta.

E. Hyposulphite of Baryta.—Crystallizes gradually in needles from a solution of sulphide of barium exposed to the air; it is slightly soluble in water. The crystals heated in a retort evolve water, hydrosulphuric acid, and sulphur, leaving a mixture of sulphide of barium and sulphate of baryta. (H. Rose, *Pogg.* 21, 437.) At a temperature of 200° in vacuo over oil of vitriol, they lose very little water; but at 170° they lose 6·14 per cent. The residue gradually heated to redness in a retort, still yields a small quantity of water, together with sulphur (but neither sulphuretted hydrogen nor sulphurous acid), and cakes together in a yellowish-white mass, consisting of sulphate and sulphite of baryta together with sulphide of barium. (Rammelsberg, *Pogg.* 56, 300.)

| | Crystallized. | | H. Rose. |
|---|---|---|---|
| BaO | 76·6 | 57·33 | 57·24 |
| $S^2O^2$ | 48·0 | 35·93 | 36·03 |
| HO | 9·0 | 6·74 | 6·73 |
| BaO, $S^2O^2$ + Aq. | 133·6 | 100·00 | 100·00 |

¶ F. Pentathionate of Baryta.—BaO, $S^5O^5$ + HO.—Soluble in water. Lenoir obtained definite crystals by mixing an aqueous solution with strong alcohol. Transparent silky prisms, which change within the liquid to large, well defined crystals. ¶

G. Tetrathionate of Baryta.—BaO, $S^4O^5$.—When hyposulphite of baryta is diffused through water and iodine added to the liquid, the hyposulphite is dissolved till the quantity of tetrathionate of baryta formed increases to such an extent that it separates in flakes, and at length renders the liquid thick. Strong alcohol takes up the iodide of barium together with the excess of iodine from the semi-fluid mass. The tetrathionate of baryta remaining in the form of powder yields, by the spontaneous evaporation of its aqueous solution, or on the addition of alcohol to that solution, beautiful hydrated crystals. These are decomposed by heat, yielding water, sulphur, and sulphurous acid, with a residue of sulphate of baryta. If the acid of the salt be converted into sulphuric acid by passing a stream of chlorine gas through its aqueous solution, the precipitate of sulphate of baryta so formed amounts to one-third as much as that produced by adding nitrate of baryta to the filtered solution. (Fordos & Gélis, *Compt. Rendus*, 15, 920.)

H. Trithionate of Baryta.—BaO, $S^3O^5$ + 2HO.—1. Free trithionic acid gives, with baryta-water, a precipitate soluble in a large quantity of water or in nitric acid. (Langlois.) ¶ 2. Obtained in brilliant plates by adding alcohol to a solution of carbonate of baryta in the acid. The salt is readily decomposed, with separation of sulphate of baryta. (Kessler, *Pogg.* 74, 249.) ¶

I. Sulphite of Baryta.—Formed by passing sulphurous acid gas into water in which carbonate of baryta is diffused; or by precipitating chloride of barium with sulphite of soda. It falls down in fine tasteless needles, and crystallizes from a solution in aqueous sulphurous acid on evaporation, in hard transparent tetrahedrons with truncated summits. (*Fig.* 14.) Scarcely soluble in water. (Fourcroy & Vauquelin, *Ann. Chim.* 24, 301.) ¶ It may be obtained in six-sided prisms by *gently heating* a solution of baryta in sulphurous acid water and leaving

it at rest for some days. The crystals contain a small quantity of water mechanically combined; they decrepitate when gently heated. (Muspratt.)

| | Calculation. | | Berzelius. | Fourcroy & Vauquelin. | Muspratt. |
|---|---|---|---|---|---|
| BaO | 76·6 | 70·53 | 69·74 | 59 | 68·73 |
| $SO^3$ | 32·0 | 29·47 | 28·84 | 39 | 28·81 |
| Water | | | 1·42 | 2 | 2·46 |
| BaO, $SO^3$ | 108·6 | 100·00 | 100·00 | 100 | 100·00 |

K. Hyposulphate of Baryta.—Hyposulphate of manganous oxide is decomposed by baryta-water (II., 174), or by aqueous solution of sulphide of barium in equivalent proportion—then filtered and evaporated. The salt crystallizes at high temperatures with 2 atoms, and at a lower temperature, never exceeding 5°, with 4 atoms of water.

*α. With 2 atoms of water.*—Shining, four-sided prisms, terminated with several faces (Gay-Lussac & Welter), and apparently belonging to the oblique prismatic system. (Heeren.) Taste bitter, and somewhat rough. The crystals are permanent in the air; decrepitate strongly when heated; and at moderately high temperatures, evolve 29·903 per cent. of water together with sulphurous acid, while 70·097 per cent. of sulphate of baryta remains behind. (Welter & Gay-Lussac.) At 8·14° it dissolves in 7·17 parts of water (Gay-Lussac), at 18° in 4·04 parts, and at 100° in 1·1 parts of water. Insoluble in alcohol. (Heeren.)

| | Calculation. | Welter & Gay-Lussac. | Heeren. |
|---|---|---|---|
| BaO | 76·6 | 46·0 | 46·03 | 45·93 |
| $S^2O^5$ | 72·0 | 43·2 | 43·41 | 43·31 |
| 2HO | 18·0 | 10·8 | 10·56 | 10·76 |
| BaO, $S^2O^5$ + 2Aq. | 166·6 | 100·0 | 100·00 | 100·00 |

*β. With 4 atoms of Water.*—Large crystals belonging to the right prismatic system (*Fig.* 44); $u : u = 102°$ and 78°; $a$ or $a^1 : u$ or $u^1 = 145°$. (Heeren.) $u : u = 101° 30'$, and 78° 30'; $a : u = 145°$; cleavage parallel to $u$. (Walchner, *Schw.* 47, 245.) It effloresces rapidly, losing half its water; does not fuse when heated; but is converted, without change of form, into 63·79 per cent. of sulphate of baryta. (Heeren, *Pogg.* 7, 172.)

| | Calculation. | Heeren. |
|---|---|---|
| BaO | 76·6 | 41·50 | 41·88 |
| $S^2O^5$ | 72·0 | 39·00 | 39·49 |
| 4HO | 36·0 | 19·50 | 18·63 |
| BaO, $S^2O^5$ + 4Aq. | 184·6 | 100·00 | 100·00 |

L. Sulphate of Baryta.—a. *Monosulphate.*—Found native as *Heavy-spar:* sometimes formed from Witherite or Baryto-calcite, which has gradually been converted from without inwards into sulphate of baryta. (Haidinger, *Pogg.* 11, 376.) Vapour of anhydrous sulphuric acid passed over heated baryta is absorbed, the temperature of the baryta rising to vivid incandescence. (Bussy, *J. Pharm.* 10, 370.) Baryta rises to bright incandescence in contact with anhydrous sulphuric acid, fused at 25° (Kuhlmann); it also becomes red-hot when mixed with oil of vitriol (Barry, *Ann. Phil.* 18, 77); only, however, when the oil of vitriol consists

of one atom of acid with a little more or a little less than one atom of water. (Kuhlmann.) Oil of vitriol of specific gravity 1·848, which contains exactly one atom of water, does not combine with baryta at ordinary temperatures; but if the baryta, when moistened with the oil of vitriol, be touched at any point with a hot iron, or a wet glass rod, combination immediately commences at that point, and is propagated throughout the mass: the same occurs on exposure to moist air. The same oil of vitriol previously mixed with a small quantity of water and cooled, immediately unites with the baryta with incandescence: if the water is in larger proportion, the latter effect does not take place. With baryta which has absorbed water from the air, pure oil of vitriol behaves as above. Even when the acid is mixed with a quantity of water sufficient to make it combine with the baryta, it remains without action on that substance, if previously mixed with alcohol, ether, or wood spirit. (Kuhlmann, *Ann. Pharm.* 27, 22.) Sulphuric acid and its salts precipitate sulphate of baryta from the aqueous solutions of all baryta-salts. The crystalline system of heavy-spar is the right prismatic (*Fig.* 49, 61, and many other forms); $u^1 : u = 101° 32\frac{1}{4}'$; $p : i = 127° 5'$, and so on; planes of cleavage parallel to $p$, $u^1$ and $u$. (Hauy.) The artificial sulphate has the form of a white powder. Specific gravity of the native sulphate = 4·446. (Mohs.) Fuses, according to Saussure, at 35° Wedgwood to a white enamel. Tasteless, and not poisonous.

| | Calculation. | | Fourcroy. | Berzelius. | Klaproth. | Kirwan. |
|---|---|---|---|---|---|---|
| BaO | 76·6 | 65·695 | 65·22 | 65·643 | 66·7 | 67 |
| $SO^3$ | 40·0 | 34·305 | 34·78 | 34·357 | 33·3 | 33 |
| BaO, $SO^3$ | 116·6 | 100·000 | 100·00 | 100·000 | 100·0 | 100 |

| | Withering. | Bucholz. | Clem. & Desorm. | Richter. | Thénard. | Chenevix. |
|---|---|---|---|---|---|---|
| BaO | 67·2 | 67·5 | 67·82 | 69 | 74·82 | 76·5 |
| $SO^3$ | 32·8 | 32·5 | 32·18 | 31 | 25·18 | 23·5 |
| BaO, $SO^3$ | 100·0 | 100·0 | 100·00 | 100 | 100·00 | 100·0 |

By ignition with charcoal it is converted into sulphide of barium, with evolution of carbonic oxide and hydrogen gases; by ignition with bisulphide of carbon, into sulphide of barium and carbonate of baryta; by fusion, or less perfectly, by boiling with carbonate of potash or soda, into carbonate of baryta; but the decomposition is only partial: in the cold, the effect is reversed. (*Vid.* Klaproth, *Beiträge* 2, 70 and 73,—Dulong, *Ann. Chim.* 82, 273,—Phillips, *Schw.* 25, 290,—Kölreuter, *Mag. Pharm.* 8, 181.)—According to John (*Schw.* 14, 412), it is completely decomposed when boiled down with a solution of potash and then fused, yielding baryta and sulphate of potash. Fused with chloride of calcium, it forms chloride of barium and sulphate of lime (*Sch.* 52); whereas chloride of barium and sulphate of lime in solution, form chloride of calcium and sulphate of baryta. Sulphate of baryta requires 43,000 parts of cold water for solution; it is not much more soluble in hot or acidulated water. Neither is it perceptibly soluble in water containing sal-ammoniac or common salt. (Brett, Wittstein, Wackenroder.) When baryta is precipitated from an aqueous solution by sulphuric acid or a sulphate, the sulphate of baryta often carries down with it other substances contained in the liquid; and these substances cannot be totally separated by washing. If the solution contains nitrate of soda, the precipitate, after being completely washed, still retains 2 per cent. of this salt; this, how-

ever, is decomposed by exposure to a red heat, after which the soda may be dissolved out by water; nitrate of baryta also (but not the chloride) is carried down in considerable quantity with the sulphate, but can be separated by washing with water. (Mitscherlich, *Pogg.* 55, 214.) Chloride of magnesium also, as well as the oxides of iron, cobalt, copper, &c. mix with the sulphate of baryta thrown down by mixing sulphate of magnesia, &c. with chloride of barium. (Berzelius, *Ann. Chim. Phys.* 14, 374.) Sulphate of baryta may be fused with chloride of sodium or chloride of barium. (Berthier.)

b. *Acid Sulphate.*—The neutral salt dissolves in oil of vitriol; groups of needles crystallize from the solution. Water decomposes them into simple sulphate of baryta which falls to the bottom, and dilute sulphuric acid.

M. Sulphide of Carbon and Barium and Hydro-sulphocarbonate of Baryta.—Crystallized monohydrosulphate of baryta rapidly combines with bisulphide of carbon, producing a lemon-yellow uncrystallizable salt. This is dissolved with difficulty by water, forming a liquid of a brownish-yellow colour, which, when mixed with more water (probably from the air it contains), passes into red. The solution evaporated in vacuo leaves small, pale-yellow, transparent crystals. A drop of water suffered to fall on these crystals produces after some minutes a red colour, which, however, on drying, again changes to a pale yellow. (Berzelius.)

## Barium and Selenium.

A. Selenide of Barium.—Formed by exposing seleniate of baryta at a red heat to a current of hydrogen gas. Soluble in water. (Berzelius.)

B. Hydroselenite of Baryta.—Hydroselenite of potash produces with baryta-salts a flesh-coloured precipitate, from which acids separate selenium; but no selenium is evolved at a red heat. (Berzelius.)

C. Selenite of Baryta.—a. *Monoselenite.* Selenious acid produces no precipitate with solutions of baryta, which at once distinguishes it from sulphurous acid. (Muspratt.)—Prepared by precipitating chloride of barium with simple selenite of potash. White powder, which seems to contain no water, does not turn reddened litmus blue. Infusible at the melting point of glass. Insoluble in water, but dissolved by selenious, hydrochloric, and nitric acids. (Berzelius.)—¶ When neutral selenite of potash is added to nitrate of baryta, decomposition takes place, and selenite of baryta is deposited in delicate, shining, plumose crystals. (Muspratt.) ¶

b. *Biselenite.*—Prepared by dissolving carbonate of baryta in aqueous selenious acid. If the liquid contains no excess of acid, it yields on spontaneous evaporation an opaque, white, granular mass of crystals; but if the quantity of acid is somewhat greater than 2 atoms, rounded grains of concentric, fibrous texture are formed on evaporation. Water dissolves the salt with difficulty; nevertheless the solution deposits it but slowly on evaporation. Ammonia precipitates the salt *a* from the liquid. (Berzelius.) At high temperatures it evolves water and white fumes of selenious acid. (Muspratt.)

| | | Salt a. | | Berzelius. |
|---|---|---|---|---|
| BaO | 76·6 | 57·7 | | 57·93 |
| $SeO^2$ | 56·0 | 42·3 | | 42·07 |
| $BaO, SeO^2$ | 132·6 | 100·0 | | 100·00 |

| | | Salt b. | | Berzelius. |
|---|---|---|---|---|
| BaO | 76·6 | 40·6 | | 40·48 |
| $2SeO^2$ | 112·0 | 59·4 | | 59·52 |
| $BaO, 2SeO^2$ | 188·6 | 100·0 | | 100·00 |

D. Seleniate of Baryta.—At a low red heat, at which the sulphate remains unchanged, this salt is reduced by hydrogen gas to selenide of barium, often with incandescence; the mass remains unchanged in appearance.—Imperfectly decomposed by sulphuric acid. It is as little soluble in water as the sulphate of baryta. (Berzelius, *Pogg.* 32, 11.)

## Barium and Iodine.

A. Iodide of Barium.—Formed when hydriodic acid gas is passed over baryta at a red heat, the combination being attended with emission of light. Monosulphide of barium dissolved in water is mixed with a saturated alcoholic solution of iodine [iodine without the alcohol might be preferable], as long as a precipitate of sulphur is formed; the colourless filtrate is boiled rapidly—so as to prevent the action of the air—almost to dryness; the mass dissolved in a small quantity of water; filtered quickly; and the filtrate evaporated to dryness in as short a space of time as possible in a glass flask. (O. Henry.) White; infusible (Gay-Lussac); greyish-white, consisting of needles. (Henry.) Heated out of contact of air, it is not decomposed; but when the air is admitted, the salt is converted into baryta and vapour of iodine. (Gay-Lussac.)

| | Calculation. | | O. Henry. |
|---|---|---|---|
| Ba | 68·6 | 35·25 | 35·17 |
| I | 126·0 | 64·75 | 64·83 |
| Ba,I | 194·6 | 100·00 | 100·00 |

Iodide of barium dissolves very readily in water, but does not deliquesce in the air. (Gay-Lussac.) It is very deliquescent. (O. Henry.) The aqueous solution yields on evaporation and subsequent cooling very fine needles of *hydrated iodide of barium* or *hydriodate of baryta*. When exposed to the air it is converted into hydriodite of baryta with precipitation of carbonate of baryta. (Gay-Lussac.) Iodide of barium is also easily dissolved by alcohol. (O. Henry.)

According to Gay-Lussac, *iodide of baryta* is formed when vapour of iodine is passed over baryta at a red heat.

B. Iodate of Baryta.—1. Precipitated when iodine is dissolved in baryta-water, iodide of barium remaining in solution. (Gay-Lussac.) 2. Aqueous solution of terchloride of iodine is saturated with carbonate of baryta [or baryta-water], and the precipitate well washed. (Grosourdy, *J. Chim. Med.* 9, 428.) 3. A concentrated solution of chloride of barium is precipitated by a solution of iodate of soda. (Rammelsberg.) The insoluble salt is washed with cold water. In combination with *water of crystallization* it forms a white granular (Gay-Lussac,)

Separates in small crystals from solution in hot nitric acid, on cooling or on the addition of ammonia. (Rammelsberg.) The water of crystallization escapes at a temperature below 200°. Heated more strongly in a porcelain retort, vapour of iodine and oxygen gas are evolved, and a residue is obtained, consisting of 46·973 per cent. of $\frac{1}{5}$ periodate of baryta. (Rammelsberg.)

$$5(BaO, IO^5) = 5BaO, IO^7 + 4I + 18O.$$

It does not detonate on red-hot charcoal, but sometimes exhibits phosphorescence. (Gay-Lussac.) Hydrochloric acid dissolves it readily, even in the cold, the liquid assuming a dark yellow colour, (probably arising from the formation of a double chloride of iodine and barium, *Filhol*,) and evolving chlorine. It dissolves with difficulty in warm nitric acid. (Rammelsberg.) It is soluble in 3·333 parts of water at 18°, and in 625 parts of boiling water. (Gay-Lussac.) Dissolves in 1746 parts of water, at 15°, and in 600 parts of boiling water. (Rammelsberg.)

| | | Anhydrous. | |
|---|---|---|---|
| BaO | 76·6 | | 31·57 |
| $IO^5$ | 166·0 | | 68·43 |
| $BaO, IO^5$ | 242·6 | | 100·00 |

| | Crystallized. | | Rammelsberg. |
|---|---|---|---|
| BaO | 76·6 | 30·45 | 96·04 |
| $IO^5$ | 166·0 | 65·98 | |
| HO | 9·0 | 3·57 | 3·96 |
| $BaO, IO^5 + HO$ | 251·6 | 100·00 | 100·00 |

C. PERIODATE OF BARYTA.—When a mixture of iodide of barium and peroxide of barium is exposed to a low red heat, a considerable quantity of periodate of baryta is formed. (Rammelsberg.)—a. *One-fifth periodate.*—Remains after heating the iodate of baryta to redness. It is freed from the iodide of barium sometimes present, but never exceeding one per cent., by washing with water. Heated in a current of hydrogen gas, it becomes strongly ignited, emitting a greenish light and fusing, and is resolved into water, iodide of barium, and free baryta; part, however, remains undecomposed, even after long continued ignition. Soluble in nitric acid, but not in water. (Rammelsberg.)

| | Calculation. | | Or: | Calculation. | | Rammelsberg. |
|---|---|---|---|---|---|---|
| 5BaO | 383 | 67·79 | 5Ba | 343 | 60·71 | 60·07 |
| $IO^7$ | 182 | 32·21 | I | 126 | 22·30 | 21·83 |
| | | | 12O | 96 | 16·99 | 18·10 |
| $5BaO, IO^7$ | 565 | 100·00 | „ | 565 | 100·00 | 100·00 |

b. *Two-fifths periodate.*—1. Formed by precipitating nitrate of baryta with monoperiodate of soda. The supernatant liquid becomes acid. (Benckiser, *Ann. Pharm.* 17, 254.)—2. By mixing a salt of baryta with diperiodate of soda dissolved in nitric acid, and precipitating the solution by ammonia.—3. By precipitating the solution of *a* in nitric acid by ammonia. Yellowish precipitate containing water, which is expelled at a temperature of 150°. Converted, for the most part, even below 100°, into iodate of baryta. (Rammelsberg, *Pogg.* 44, 572.) Not soluble in water, but easily soluble in weak nitric acid. (*Benckiser.*)

| | Anhydrous. | |
|---|---|---|
| 5BaO | 383 | 51·27 |
| $2IO^7$ | 364 | 48·73 |
| $5BaO, 2IO^7$ | 747 | 100·00 |

| | Hydrated. | | Rammelsberg. | |
|---|---|---|---|---|
| 5BaO | 383 | 48·36 | 48·23 | |
| $2IO^7$ | 364 | 45·96 | 46·69 | |
| 5HO | 45 | 5·68 | 5·08 | |
| $5BaO, 2IO^7 + 5Aq.$ | 792 | 100·00 | 100·00 | |

## Barium and Bromine.

A. Bromide of Barium.—Formed by neutralizing aqueous hydrobromic acid with baryta-water or carbonate of baryta (Balard); or by decomposing sulphide of barium dissolved in water with hydrobromic acid (Löwig), evaporating the solution to dryness, and igniting the residue.

Bromide of barium dissolves easily in water, and gives, on evaporation and subsequent cooling, crystals of *bihydrated bromide of barium*, or *mono-hydrated hydrobromate of baryta*. They are transparent, colourless, rhombic tables, isomorphous with those of chloride of barium, and permanent in the air; their edges are replaced by the faces of a rhombic octohedron. (Rammelsberg, *Pogg.* 55, 237.) Slender needles united in opaque, warty masses, fusing when heated. (Balard.) Tastes like chloride of barium, but rougher. Carbonic acid passed through an aqueous solution [containing air?] colours it yellow, from formation of hydrobromite of baryta, carbonate of baryta being precipitated. (Löwig.) Bromide of barium dissolves readily in absolute alcohol, in which the chloride is insoluble. (Hünefeld, Piria, *J. Chem. Med.* 14, 65.) In this way, bromine may be separated from chlorine. (O. Henry, *J. Pharm.* 28, 214.)

| | Anhydrous. | |
|---|---|---|
| Ba | 68·6 | 46·67 |
| Br | 78·4 | 53·33 |
| Ba, Br | 147·0 | 100·00 |

| | Crystallized. | | Rammelsberg. | Löwig. |
|---|---|---|---|---|
| BaBr | 147 | 89·09 | 88·68 | 94 |
| 2HO | 18 | 10·91 | 11·32 | 6 |
| BaBr, 2Aq. | 165 | 100·00 | 100·00 | 100 |

B. Hypobromite of Baryta?—By dissolving a small quantity of bromine in baryta-water, a colourless liquid is obtained which deposits but little bromate of baryta, and when evaporated in vacuo, deposits yellow crystalline scales, which heat bibulous paper on which they are placed to dry, to such a degree that it takes fire. The liquid soon loses its bleaching properties when exposed to light or heat, also on the addition of an excess of bromine, which produces an abundant precipitate of bromate of baryta. (Balard.)

C. Bromate of Baryta.—1. Formed by mixing baryta-water with excess of bromine. Bromate of baryta falls down, bromide of barium remaining dissolved. (Löwig.) 2. By mixing baryta-water with chloride of bromine. (Balard.) 3. By precipitating chloride of barium dissolved in a small quantity of water, by a solution of bromate of potash.

(Löwig.) 100 parts of bromate of potash are dissolved in one portion of boiling water and 74 parts of crystallized chloride of barium or 160 parts of anhydrous acetate of baryta (which is to be preferred on account of the ease with which the acetate of potash can be washed out), in another portion, and the two solutions are mixed. (Rammelsberg.)—Needles (Balard); rectangular prisms, with truncated edges. (Rammelsberg.) The crystals do not lose all their water till they are heated above 200°. When more strongly heated, the residue is at once resolved, with violent escape of gas and formation of flame, into oxygen gas and bromide of barium, without previous formation of a perbromate of baryta. (Rammelsberg.) Detonates on ignited charcoal with a greenish-coloured flame. (Balard.) Oil of vitriol or hydrochloric acid decomposes it, with separation of bromine. Soluble in 130 parts of cold, and in 24 parts of boiling water. (Rammelsberg, *Pogg.* 52, 81 and 86.)

| | Anhydrous. | |
|---|---|---|
| BaO | 76·6 | 39·28 |
| $BrO^5$ | 118·4 | 60·72 |
| BaO, $BrO^5$ | 195·0 | 100·00 |

| | Crystallized. | | Rammelsberg. |
|---|---|---|---|
| BaO | 76·6 | 37·55 | 37·56 |
| $BrO^5$ | 118·4 | 58·04 | 58·03 |
| HO | 9·0 | 4·41 | 4·41 |
| BaO, $BrO^5$ + Aq. | 204·0 | 100·00 | 100·00 |

## Barium and Chlorine.

A. Chloride of Barium.—Baryta heated in chlorine gas is converted into chloride of barium, with separation of a half-volume of oxygen gas (H. Davy); heated in hydrochloric acid gas, it is rapidly converted into fused chloride of barium, with evolution of heat and a reddish light, water being formed at the same time. (Chevreul, *Ann. Chim.* 84, 285.) Baryta emits light when hydrochloric acid is dropped upon it in the dark. (Heinrich.) Chloride of barium is obtained in the anhydrous state, by heating the hydrated chloride or hydrochlorate of baryta to redness.

White mass, fusing at a full red heat, and translucent after solidification; sp. gr. = 3·7037 (Karsten), 3·8 (Richter), 3·86 to 4·156. (Pol. Boullay.) Tastes bitter, sharp, and unpleasant; excites nausea, and acts on the system as a strong poison. Heated by itself, it does not become alkaline till after fusion; but when heated in aqueous vapour it becomes alkaline below the melting point, and evolves hydrochloric acid. (E. Kraus, *Pogg.* 43, 140.) By ignition with sulphur it is partly converted into sulphide of barium. (A. Vogel, *Schw.* 21, 72.) In the state of solution, nitrate of potash or soda decomposes it by double affinity. (Karsten.) It is not decomposed at ordinary temperatures by vapour of anhydrous sulphuric acid. (H. Rose, *Pogg.* 38, 120.)

| | Calculation. | | Turner. |
|---|---|---|---|
| Ba | 68·6 | 66 | 65·984 |
| Cl | 35·4 | 34 | 34·016 |
| Ba, Cl | 104·0 | 100 | 100·000 |

| Or: | Calculation. | | Berzelius. | Val. Rose. | Kirwan. |
|---|---|---|---|---|---|
| BaO ..... | 76·6 .... | 73·7 .... | 73·63 .... | 75·69 .... | 76·2 |
| $MuO^2$ ..... | 27·4 .... | 26·3 .... | 26·37 .... | 24·31 .... | 23·8 |
| $BaO, MuO^2$ .... | 104·0 .... | 100·0 .... | 100·00 .... | 100·00 .... | 100·0 |

*Bi-hydrated Chloride of Barium*, or *Mono-hydrated Hydrochlorate of Baryta.—Terra ponderosa salita.*—Fused chloride of barium becomes opaque in the air from absorption of water; 100 parts heated to redness, but not fused, gain from the air in a few days 17·49 per cent. (2 At.) of water. (Von Blücher.) The combination of chloride of barium with water is attended with rise of temperature.

*Preparation.*—1. By decomposing aqueous solution of sulphide of barium with hydrochloric acid. A filtered solution of sulphide of barium (III., 147) is mixed with hydrochloric acid till the yellow colour disappears and the liquid strongly reddens litmus; it is then boiled for some time in a porcelain basin, to drive off all the sulphuretted hydrogen, and condense the sulphur—which would otherwise pass through the filter—then filtered, evaporated, and cooled till it crystallizes.—2. By saturating hydrochloric acid with carbonate of baryta. For this purpose, either the native carbonate or the artificially prepared carbonate is used. The latter is obtained either by the method already described (III., 139, 2 and 3), or by boiling 1 part of finely powdered heavy-spar for some hours with 1½ to 2 parts of carbonate of potash dissolved in water. It is better, however, to fuse it with carbonate of potash. In both cases, part of the heavy-spar is decomposed, but by no means the whole, even when the carbonate of potash is used in large excess. The products are carbonate of baryta and sulphate of potash. The mass is thoroughly washed with boiling water, which takes up the sulphate and carbonate of potash; if cold water were used, the carbonate of baryta would, according to Kölreuter's experiments, be again converted into sulphate. From the powder, after exhaustion with water, hydrochloric acid withdraws the baryta which is in union with carbonic acid, leaving the undecomposed sulphate behind. As the heavy-spar is not usually free from oxide of iron, this substance enters into the solution, and must be separated, either by evaporation, ignition, solution, and filtration—or by boiling the liquid with an excess of carbonate of baryta—or by mixing baryta-water with it.—3. Two parts of pounded heavy-spar are fused with 1 part of chloride of calcium; the mass, after being poured out and solidified, is powdered and quickly dissolved in 6 times its weight of boiling water; and the solution of chloride of barium rapidly filtered from the gypsum. (Von Driessen.) (*Sch.* 52.) The fusion is performed in an earthen crucible heated in a powerful wind-furnace. When water is added, the affinities are reversed,—the chloride of barium and sulphate of lime being again resolved into chloride of calcium and sulphate of baryta; hence the solution of the chloride of barium must be filtered as quickly as possible from the sulphate of lime. The powdered mass should therefore be thrown into an iron vessel containing water already boiling, and the liquid immediately poured upon a filter of linen or other material which allows it to pass through rapidly. The filtrate always contains chloride of calcium, mixed with the chloride of barium; and this salt remains in the mother-liquor after the chloride of barium has crystallized out. The crystals of chloride of barium must be separated from it either by re-crystallization or by washing with alcohol. By the *improved* process of Duflos, these difficulties are obviated (*Schw.* 65, 236).

An intimate mixture of 30 parts of finely divided heavy-spar, 18 parts of chloride of calcium, and 7 parts of charcoal (or, according to his more recent process, 4 parts of heavy-spar, 2 parts of chloride of calcium, and 1 part of lampblack) are ignited in a crucible as long as flames of carbonic oxide are seen to proceed from the semi-fluid mass. It is then scraped out with an iron spoon, powdered fine, boiled with 10 parts of water, and filtered. The sulphate of lime is converted by the charcoal into sulphide of calcium, and thus the decomposition of the chloride of barium is prevented. The quantity of chloride produced this way is nearly equal to that of the heavy-spar used. The chloride of calcium may be dissolved in water and evaporated, the solution mixed with the powdered sulphate of baryta and lampblack; evaporated to dryness, with constant stirring, in an iron vessel; and the residue put into the crucible. (Duflos.) Mitscherlich adds iron-filings in addition to the carbon.

The salt is purified by re-crystallization, sometimes also by exposure to a red heat and treatment with alcohol.

*Impurities.—Chloride of Strontium:* inasmuch as several kinds of heavy-spar contain small quantities of sulphate of strontia; separated by means of alcohol.—*Chloride of Calcium:* sometimes present in the heavy-spar, or originating from the method of preparation (in the third method, for instance); likewise removed by alcohol. Both chloride of strontium and chloride of calcium colour the flame of alcohol red; but the latter is precipitated from a dilute solution by oxalic acid, while the chloride of strontium is not.—*Chloride of aluminum and sesqui-chloride of iron:* arising from the clay and oxide of iron mixed with the heavy-spar; most likely to be present in the chloride of barium prepared by the second method; decomposed by exposure to a red heat; precipitated by baryta-water, or carbonate of baryta; dissolved out by alcohol.—*Cyanide of barium* [probably cyanide of iron and barium]: found in the commercial salt by Buchner (*Repert.* 41, 405); gives a blue precipitate with salts of ferric oxide.

Transparent, colourless tables, permanent in the air. Belonging to the right prismatic system; having the form of the crystals of heavy-spar, only with different angles. (*Figs.* 51 and 52.) $u^1 : u = 92° 30'$; $u : a = 156° 20'$; $p : i = 122° 40'$; $p : ii = 142$; $p : y = 140$. (Von Kobell, *Schw.* 64, 298; also Haidinger, *Edinb. J. of Sc.* 1, 101.) Sp. gr. = 3·0497. (Karsten.) Decrepitates in the fire.

| | Calculation. | | J. Davy. | Pleischl. | Richter. |
|---|---|---|---|---|---|
| Ba | 68·6 | 56·23 | 83·91 | 84·3 | 82·25 |
| Cl | 35·4 | 29·02 | | | |
| 2HO | 18·0 | 14·75 | 16·09 | 15·7 | 17·75 |
| BaCl, 2HO | 122·0 | 100·00 | 100·00 | 100·0 | 100·00 |

| Or: | Calculation. | |
|---|---|---|
| BaO | 76·6 | 62·79 |
| HCl | 36·4 | 29·83 |
| HO | 9·0 | 7·38 |
| BaO, HCl + Aq. | 122·0 | 100·00 |

| Or: | Calculation. | | Berzelius. | Aiken. | Kirwan. | Bucholz. |
|---|---|---|---|---|---|---|
| BaO | 76·6 | 62·79 | 61·852 | 62·47 | 64 | 63·74 |
| $MuO^2$ | 27·4 | 22·46 | 23·349 | 22·93 | 20 | 20·26 |
| 2HO | 18·0 | 14·75 | 14·799 | 14·60 | 16 | 16·00 |
| | 122·0 | 100·00 | 100·000 | 100·00 | 100 | 100·00 |

100 parts of water at 0° dissolve 32·62 parts of chloride of barium, and 0·2711 parts for every degree above 0°; 100 parts of water at 15·6 dissolve 43·5, and at 105·5°, 78 parts of the crystallized chloride. (Gay-Lussac.) One part of crystallized chloride of barium dissolves at 18·1° in 2·257 parts of water, forming a solution of specific gravity 1·2851. (Karsten.) Specific gravity of a saturated solution at 8° = 1·270. (Anthon; *vid.* also Brandes & Melm, *Repert.* 14, 97.) Water acidulated with hydrochloric acid dissolves less than pure water, and concentrated aqueous hydrochloric acid hardly any; so that a saturated solution in water is precipitated by it. Hot absolute alcohol dissolves only $\frac{1}{100}$ part of the crystals, but more if it contains water. ¶ According to Friesenius (*Ann. Pharm.* 59, 117), one part of the salt dissolves in 8108 parts of alcohol of 99·3 per cent. at 14°, and in 4857 parts of the same alcohol at a boiling heat. ¶

B. Hypochlorite of Baryta?—One atom of hydrate of baryta absorbs one atom of chlorine gas; the compound is completely decomposed by exposure for two days to an atmosphere of carbonic acid. (Grouvelle, *Ann. Chim. Phys.* 17, 40.)

¶ C. Chlorite of Baryta.—Caustic baryta combines slowly with chlorous acid, forming an easily soluble salt. The salt may be obtained nearly free from chloride of barium by quickly evaporating the solution till a film is formed on the surface, and then placing it in vacuo. If the solution is evaporated slowly, crystals of chlorate of baryta are first obtained, but the mother-liquid afterwards deposits a considerable quantity of undecomposed chlorite. The salt undergoes decomposition at 235°, being resolved into a mixture of chloride of barium and chlorate of baryta.

| | Calculation. | | | Millon. |
|---|---|---|---|---|
| BaO ..... | 76·6 | .... | 56·32 | ..... 55·95 |
| $ClO^3$ ..... | 59·4 | .... | 43·68 | ..... 44·04 |
| | 136·0 | .... | 100·00 | ..... 99·99 |

Carbonate of baryta is not decomposed by chlorous acid. ¶

D. Chlorate of Baryta.—1. An aqueous solution of chloric acid is saturated with baryta-water or carbonate of baryta.—*a.* Wheeler (*Ann. Chim. Phys.* 7, 74) mixes a hot solution of chlorate of potash with hydrofluosilicic acid, so that the latter may somewhat predominate (which may be known by the liquid still producing a precipitate of silica with ammonia); heats the mixture gently for some minutes, when the double fluoride of silicium and potassium falls down in a gelatinous form; filters from this precipitate, and saturates the liquid, which contains chloric acid and excess of hydrofluosilicic acid, with carbonate of baryta. After this, nothing but chlorate of baryta remains dissolved; it is filtered and evaporated to the crystallizing point.—*b.* Duflos (*N. Br. Arch.* 23, 306) adds to a solution of 27 parts of chlorate of soda in 54 parts of water, another solution containing 38 parts of tartaric acid in 38 parts of water; throws this mixture into double the quantity of nearly absolute alcohol; and after 24 hours, filters from the crystallized acid tartrate of soda: he then neutralizes the liquid with carbonate of baryta; allows the alcohol to evaporate; filters, and evaporates to the crystallizing point.—2. Chlorine gas is passed through warm water in which baryta is diffused and partly dis-

solved. The greater part of the chloride of barium is suffered to crystallize out, and the rest is removed by adding phosphate of silver to the solution in the exact quantity required. The liquid ought not to become turbid by the addition of hydrochloric acid or nitrate of silver. (Chenevix, Vauquelin.) The addition of acetic acid somewhat accelerates the action of the phosphate of silver on the chloride of barium; but the chlorate of baryta then becomes mixed with acetate, and detonates violently when heated. (Vauquelin, *Schw.* 14, 111.)

Transparent, colourless (rhomboidal: *Wächter*), four-sided prisms, sometimes with oblique, sometimes with perpendicular terminal faces; taste rough and acrid. (Vauquelin.)—The anhydrous salt evolves, when heated, 39 per cent. of oxygen gas, leaving chloride of barium mixed with free baryta. (Vauquelin.) ¶ Evolves water at 120°, oxygen at 250°, and fuses at a temperature above 400°. (Wächter, *Ann. Pharm.* 52, 231.) ¶ Detonates powerfully with combustible bodies, and when heated with sulphur, gives a green flame (Duflos): when oil of vitriol is poured over it, a powerful flashing light is emitted. (Chenevix.) Dissolves in 4 parts of cold, and in a smaller quantity of hot water. (Chenevix.) It is insoluble in alcohol. (Vauquelin.)

| | Anhydrous. | | Vauquelin. | Chenevix. |
|---|---|---|---|---|
| BaO | 76·6 | 50·39 | 46 to 47 | 47·3 |
| $ClO^5$ | 75·4 | 49·61 | 54 „ 53 | 52·7 |
| BaO, $ClO^5$ | 152·0 | 100·00 | 100 „ 100 | 100·0 |

According to Chenevix the crystals contain 10·8 per cent. of water.

D. Perchlorate of Baryta.—1. An aqueous solution of perchloric acid is saturated with baryta or its carbonate.—2. Double fluoride of silicium and zinc is prepared from carbonate of zinc and gaseous fluoride of silicium, and converted into perchlorate of zinc (*vid.* perchlorate of zinc) by boiling in water with perchlorate of potash. From the solution of this salt the oxide of zinc is precipitated by baryta-water, and the liquid filtered and evaporated. (O. Henry, *J. Pharm.* 25, 268; also *Ann. Pharm.* 31, 345.)—Long prisms.—The dried salt exposed to a red heat, leaves 60 per cent. of chloride of barium. It deliquesces in the air, and dissolves readily in water and alcohol. Paper saturated with the aqueous solution, then dried and set on fire, burns with a green flame. (Serullas, *Ann. Chim. Phys.* 46, 303.)

## Barium and Fluorine.

A. Fluoride of Barium.—Precipitated on mixing hydrofluoric acid with baryta-water, or the double fluoride of hydrogen and sodium with nitrate of baryta. (Gay-Lussac & Thénard.) Freshly precipitated carbonate of baryta is digested while still moist with excess of aqueous solution of hydrofluoric acid, and the liquid containing the uncombined acid, together with a small quantity of dissolved fluoride of barium, poured off. (Berzelius.) Forms a white powder; or if obtained by evaporating the aqueous solution, a fine granular crystalline crust. (Berzelius.) Unalterable at a red heat. Insoluble in water, but readily soluble in hydrochloric, nitric, or aqueous hydrofluoric acid. (Gay-Lussac & Thénard.)

Slightly soluble in water: on evaporating a solution of it in hydrofluoric acid, it is left behind in its original state. No heat is evolved on dissolving it in aqueous hydrofluoric acid, unless it contains silica. (Berzelius, *Pogg.* 1, 18.)

| | Calculation. | | | | Berzelius. |
|---|---|---|---|---|---|
| Ba | 68·6 | .... | 78·58 | Baryta | 87·47 |
| F | 18·7 | .... | 21·42 | Hypothet. anhydrous hydfluor. acid | 12·53 |
| BaF | 87·3 | .... | 100·00 | | 100·00 |

B. HYDRATED FLUOBORIDE OF BARIUM.—Carbonate of baryta is added in small portions to an aqueous solution of tetrahydrofluate of boracic acid as long as it is dissolved. If too much baryta were added, fluoride of barium would be formed and all the boracic acid set free. On evaporating the solution, the boracic acid which may have been present in excess crystallizes out first, and when the liquid has attained a syrupy consistence, the fluoboride of barium separates. Long rectangular four-sided prisms and needles, often with step-like depressions. Tastes like the other salts of baryta, but not acid, though it reddens litmus. Loses water at a temperature of 40°, effloresces on the surface. On exposure to a red heat it loses, first liquid hydrofluate of boracic acid, then gaseous fluoride of boron, and leaves fluoride of barium. Alcohol decomposes it into an acid salt which dissolves, and a pulverulent basic salt which remains undissolved. It is easily soluble in water, and deliquesces in a moist atmosphere. (Berzelius.)

| | Crystallized. | | | Berzelius. |
|---|---|---|---|---|
| BaF | 87·3 | .... | 50·69 | 39·51 |
| $BF^3$ | 66·9 | .... | 38·85 | |
| 2HO | 18·0 | .... | 10·46 | 10·42 |
| $BaF, BF^3, 2Aq.$ | 172·2 | .... | 100·00 | |

## BARIUM AND NITROGEN.

A. NITRITE OF BARYTA.—1. Nitrate of baryta is heated to low redness, but not too long; otherwise a considerable quantity of free baryta will be formed. The residue is dissolved in water—the liquid evaporated to dryness—redissolved—filtered from carbonate of baryta—and evaporated to the crystallizing point. (Hess, *Pogg.* 12, 260.) ¶ Fischer (*Pogg.* 77, 115) dissolves the residue in water, precipitates free baryta by a current of carbonic acid, and nitrate of baryta by the addition of alcohol; on cooling, the whole of the nitrate separates. ¶—2. Baryta-water is saturated with the vapour evolved by heating fuming nitric acid—evaporated—the dry mass exhausted with a small quantity of water, which leaves the nitrate of baryta behind, and the liquid evaporated. (Fritzsche, *Pogg.* 19, 179.) It crystallizes like nitrate of baryta. (Hess.) Crystallizes in slender needles, in six-sided regular prisms, or in dense prisms belonging to the regular system. (Fischer.) The crystals are permanent in the air (Mitscherlich), and soluble in dilute alcohol. (Fischer.)

| | Crystallized. | | | Hess. |
|---|---|---|---|---|
| BaO | 76·6 | .... | 61·97 | 61·52 |
| $NO^5$ | 38·0 | .... | 30·74 | |
| HO | 9·0 | .... | 7·29 | |
| $BaO, NO^5 + Aq.$ | 123·6 | .... | 100·00 | |

Hess regards these crystals as a bihydrated compound of nitric oxide and baryta = $BaO,NO^2 + Aq$. He finds that the water cannot be expelled by merely heating the crystals.

B. NITRATE OF BARYTA.—Baryta moistened with nitric acid emits light visible in the dark. (Heinrich.)

*Preparation.* Similar to that of the chloride. (III. 158.) If the nitric acid be sufficiently dilute, and added gradually, stirring all the while, it suffers no decomposition by contact with the aqueous solution of sulphide of barium, or by the action of the nascent sulphuretted hydrogen. Mohr (*Ann. Pharm.* 25, 290) mixes a hot filtered solution of sulphide of barium with a concentrated solution of nitrate of soda; on cooling, nearly all the nitrate of baryta crystallizes out, and may be freed from adhering sulphide of sodium by washing with cold water and recrystallization. According to Wittstein, however (*Repert.* 66, 69), the sulphide of barium obtained from 10 parts of heavy-spar and 2 parts of charcoal, is but very imperfectly decomposed when mixed with 7 parts of Chili saltpetre; the crystals which appear on cooling contain but a small quantity of nitrate of baryta, and consist for the most part of sulphide of barium [baryta?], still requiring to be decomposed by nitric acid. Duflos adds to a solution of 4 parts of crystallized chloride of barium in 8 parts of hot water, a hot solution of 3 parts of Chili saltpetre in 3 parts of water—allows the mixture to cool, stirring all the while—drains the crystals—washes them by a stream of cold water—and purifies them by recrystallization.—[These niceties, however, are unnecessary.] Translucent white octohedrons and cubic octohedrons permanent in the air (*Fig.* 2 and 4); of specific gravity 3·1848 (Karsten); and having a sharp, rough taste. The salt decrepitates in the fire, and fuses at a low temperature. At a red heat it evolves oxygen and nitrogen gases, and vapours of hyponitric acid, leaving pure baryta. Detonates but slightly with combustible bodies, and with a yellowish white light on ignited charcoal. Water dissolves it with slight reduction of temperature. One part of the salt at 0° requires 20 parts; at 15°, 12·5; at 49°, 5·9; at 86°, 3·4; and at 101·6°, 2·8 parts of water for solution. (Gay-Lussac.) It dissolves at 20° in 11·66 parts of water, yielding a liquid of specific gravity 1·0678. (Karsten.) In water containing nitric acid the nitrate of baryta is much less soluble than in pure water, and in concentrated nitric acid it does not dissolve at all; it is therefore precipitated from an aqueous solution by nitric acid, and carbonate of baryta is not attacked by this acid in a concentrated form. (Mitscherlich, *Pogg.* 18, 159.) Insoluble in alcohol.

| | Crystallized. | | Berzelius. | Clem. & Desormes. | Richter. |
|---|---|---|---|---|---|
| BaO | 76·6 | 58·6 | 58·4 | 60 | 61·3 |
| $NO^5$ | 54·0 | 47·4 | 41·6 | 40 | 38·7 |
| $BaO,NO^5$ | 130·6 | 100·0 | 100·0 | 100 | 100·0 |

C. CARBONATE OF BARYTA AND AMMONIA?—Aqueous ammonia, a small portion of which is combined with carbonic acid, is not rendered turbid by baryta-water or chloride of barium, except when heated, or when left to stand for many days; so likewise chloride of barium is not completely precipitated by carbonate of ammonia in the cold. In all these cases, the carbonic acid is completely precipitated in combination with the baryta, on the application of heat. (A. Vogel, *Ann. Chim.* 89, 131; and *Schw.* 33, 204.)

## Barium and Potassium.

A. Carbonate of Baryta and Potash.—Carbonate of baryta dissolves slightly in aqueous solution of carbonate of potash. (Wackenroder, *Ann. Pharm.* 24, 30.)

B. Sulphide of Potassium and Barium.—When 5 parts of sulphate of baryta and 5 parts of sulphate of potash are exposed to a white heat in a charcoal crucible, 5·6 parts of this compound are obtained; consequently more than half the sulphide of potassium volatilizes, and 35·7 parts remain in union with 64·3 parts of sulphide of barium. Dark flesh-coloured, translucent, crystalline-granular, fused, and somewhat spongy mass, dissolving perfectly in water, with slight disengagement of heat. (Berthier, *Ann. Chim. Phys.* 22, 244.)

C. Nitrate of Baryta and Potash.—When nitrate of baryta is dissolved in a saturated solution of nitre, or nitre in a saturated solution of nitrate of baryta, a compound of the two salts in atomic proportion falls down. The saturated solutions mix without producing any precipitate. (Karsten, *Schriften der Berl. Akad.* 1841.)

## Barium and Sodium.

96·6 parts (1 At.) of *Carbonate of Baryta* form with 53·2 parts (1 At.) of dry *Carbonate of Soda*, at a strong red heat, a clear liquid as thin as water, and becoming crystalline as it cools. (Berthier, *Ann. Chim. Phys.* 38, 246.)

One part of *Baryta* heated to redness with 2 parts of *Carbonate of Soda*, gives a light green, semi-vitreous, imperfectly united mass. (Guyton-Morveau.) Baryta or carbonate of baryta fused with carbonate of soda before the blowpipe on charcoal sinks into the charcoal. (Berzelius.)

One part of *Baryta* gives with 2 parts of *Borax* a clear slightly coloured glass. (Guyton-Morveau.) On charcoal, before the blowpipe, a transparent glass is obtained, which remains clear when cold, if the baryta is used in small quantity, but becomes cloudy by interrupted blowing (technically, *flaming*). When more baryta is used, a milk-white excrescence forms at the bottom on cooling; and with a still larger proportion, the glass becomes milky from the bottom, and at last forms a perfectly opaque and white enamel. (Berzelius.)

One part of *Baryta* gives a clear glass with 2 parts of ordinary *Diphosphate of Soda*. (Guyton-Morveau.)

*Baryta* heated with *Phosphate of Soda and Ammonia*, on charcoal before the blowpipe, froths up and fuses to a clear glass, which continues clear after cooling, when but little baryta is present; but with a larger quantity becomes partially milk-white, and with a still larger proportion, enamel-like throughout. (Berzelius.)

¶ Pyrophosphate of Soda and Baryta.—6 ($2BaO, PO^5$) + $2NaO$, $PO^5$ + 6Aq. Prepared, according to Baer (*Pogg.* 75, 152) and Ludwig (*Arch. der Pharm.* 66, 265), by gradually adding chloride of barium to a

boiling solution of pyrophosphate of soda; the solution remains alkaline. The precipitate obtained is amorphous, and must be washed with water containing ammonia, because it is to a certain extent soluble in pure water. It is insoluble in pyrophosphate of soda, but readily dissolves in hydrochloric acid.

METAPHOSPHATE OF SODA AND BARYTA.—Prepared by mixing chloride of barium and metaphosphate of soda in the reverse proportions to those required for the preparation of metaphosphate of baryta. (*Vid.* Fleitmann & Henneberg's method, p. 146.) Crystallizes in fine stellated groups, and is much more soluble in water than metaphosphate of baryta itself. The crystals dried in the air contain 8 atoms of water.

| | Calculation. | | Fleitmann & Henneberg. |
|---|---|---|---|
| 2BaO | 153·2 | 38·28 | 38·74 |
| NaO | 31·0 | 7·75 | 7·58 |
| $3PO^5$ | 216·0 | 53·97 | 54·03 |
| $2BaO, NaO, 3PO^5$ | 400·2 | 100·00 | 100·35 |

(Fleitmann & Henneberg, *Ann. Pharm.* 65, 304.) ¶

83·6 parts (1 At.) of *Sulphide of Barium* fused with 53·2 parts (1 At.) of *Dry Carbonate of Soda*, yield a light-brown, opaque mass, having a granular fracture: water withdraws sulphide of sodium from it and leaves carbonate of baryta. (Berthier.)

116·6 parts (1 At.) of sulphate of baryta with 71·6 parts (1 At.) of dry carbonate of soda (or 1 atom of carbonate of baryta with 1 atom of sulphate of soda) forms a mixture which fuses readily, and after cooling appears white, opaque, and stony, with an irregular and slightly crystalline fracture. (Berthier.)

One atom of *Sulphate of Baryta* heated to whiteness with 1 atom of *Monosulphide of Sodium*, fuses to a tolerably thin paste, which when cold becomes olive-green, opaque, and dense, with a dull granular fracture, and gives up sulphide of sodium to water. (Berthier.)

116·6 parts (1 At.) of *Sulphate of Baryta* heated to whiteness with 71·2 parts (1 At.) of anhydrous sulphate of soda fuses completely, and solidifies to a white opaque mass, of crystalline-granular fracture. (Berthier.)

98·6 parts (1 At.) of *Carbonate of Baryta* heated with 58·6 parts (1 At.) of *Chloride of Sodium* fuses rapidly to a clear liquid, which exhales vapour of chloride of sodium, and solidifies to a white translucent mass, having a scaly uneven fracture. (Berthier.)

116·6 parts (1 At.) of *Sulphate of Baryta* fuses very easily when heated with 58·6 parts (1 At.) of *Chloride of Sodium*, and gives on cooling a somewhat translucent, dense, homogeneous mass, having an irregular crystalline fracture. (Berthier, *Ann. Chim. Phys.* 43, 302.)

## BARIUM AND BARIUM.

98·6 parts (1 At.) of *Carbonate of Baryta* heated to redness with 1·04 parts (1 At.) of *Chloride of Barium* yield a clear, thin liquid, which solidifies to a white transparent mass, of scaly crystalline fracture. (Berthier, *Ann. Chim. Phys.* 38, 253; Döbereiner, *Pogg.* 15, 240.)

If hydrated phosphoric acid is exposed to a red heat in contact with chloride of barium, and the excess of the latter dissolved out from the cold mass by water, there remains a compound of *Phosphate of Baryta* with *Chloride of Barium*, in various proportions, however, according to the analyses *a*, *a:* if carbonate of ammonia be thrown into the crucible at the end of the ignition, the proportions *b*, *b*, *b*, *b*, are obtained. (H. Rose.)

| | *a.* | *a.* | *b.* | *b.* | *b.* | *b.* |
|---|---|---|---|---|---|---|
| Baryta | 57·07 | 66·40 | 59·74 | 64·16 | 61·86 | 60·14 |
| Phosphoric acid | 29·09 | 23·09 | 31·23 | 26·09 | 34·04 | 36·18 |
| Chloride of barium | 13·84 | 10·51 | 9·03 | 9·75 | 4·10 | 3·68 |
| | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

One atom of *Sulphide of Barium* fuses with one atom of *Chloride of Barium* to a thin paste, which when cold assumes the colour of kermes mineral, and becomes opaque, with a slightly scaly and shining fracture.—With 2 atoms of sulphide of barium a tough mass is obtained, becoming reddish-brown, opaque, and dense, when cold, and exhibiting a dull fracture. (Berthier, *Ann. Chim. Phys.* 43, 302.)

By melting together one atom of *Sulphate of Baryta* with one atom of *Chloride of Barium*, a white very translucent mass is obtained, of scaly, laminated fracture. With 2 atoms of sulphate of baryta it exactly resembles statuary marble. (Berthier.)

Fluoride of Barium with Chloride of Barium.—Precipitated when chloride of barium is mixed with hydrofluate of soda or potash, or when ammonia is added to a solution of fluoride of barium in aqueous hydrochloric acid. White powder, or—when obtained by evaporating the solution—granular crystals, which suffer no loss of weight by exposure to a red heat. Water, which dissolves this compound more readily than the pure fluoride of barium, effects a partial decomposition, as it takes up the chloride of barium in preference to the fluoride. (Berzelius, *Pogg.* 1, 19.)

| | Calculation. | | Or: | | |
|---|---|---|---|---|---|
| BaCl | 104·0 | 54·36 | 2Ba | 137·2 | 71·72 |
| BaF | 87·3 | 45·64 | Cl | 35·4 | 18·51 |
| | | | F | 18·7 | 9·77 |
| BaCl, BaF | 191·3 | 100·00 | | 191·3 | 100·00 |

Compound of Nitrate and Phosphate of Baryta.—Formed by mixing nitrate of baryta and phosphate of ammonia, and appears as a gelatinous precipitate, very difficult to wash, and requiring therefore to be freed from the mother-liquor by pressure. It gives up the nitrate of baryta to boiling water, the phosphate remaining undissolved. (Berzelius, *Ann. Chim. Phys.* 2, 162.)

*Other compounds of Barium.*—With iron, copper, mercury, and silver.

CHAPTER V.

# STRONTIUM.

Hope. Account of a mineral from Strontian, &c. *Transactions of the Royal Society of Edinburgh*, 4, 3.
Klaproth. *Crell. Ann.* 1793, 2, 189, and 1794, 1, 99.
Kirwan. *Crell. Ann.* 1795, 2, 119 and 205.
Vauquelin. *Ann. Chim.* 29, 270; also *Scher. J.* 3, 652.
Stromeyer. *Schw.* 19, 229; also *Gilb.* 54, 245.

*History.*—The native carbonate of strontia, discovered in 1787 at Strontian, was at first regarded as carbonate of baryta. Crawford's supposition, published in 1790, that this mineral contained a peculiar earth, was confirmed in 1792 by Hope, and in 1793 by Klaproth. Sir H. Davy in 1808 first obtained from it the metal strontium.

*Sources.*—As sulphate of strontia and as carbonate of strontia; in small quantities in Arragonite and Brewsterite; and in very minute proportions in the mineral waters of Karlsbad, Königswart, Kaiser-Frauzensbrunn, and the salt spring at Eger (Berzelius, *Gilb.* 74, 145, and 290; *Pogg.* 4, 250) in those of Marienbad (Steinmann), of Bilin (Reuss), of Luhatschiwitz in Bohemia (Planiava), of Ernabrunn in the Harz (Bley), of Pyrmont (Brandes), of Selters (O. Henry), of Kissingen and of Marienfels near Nasstädten (Kastner), of Ems (Gmelin), of Lavey near Bex (Baup), of Vic-sur-Serre and Galmier (O. Henry), of St. Allyre (Girardin), of Bulgneville (Braconnot), and of Hammam Berda and Hammam Mascoutin in Algiers (Tripier).

*Preparation.* Similar to that of barium according to the first and second methods. The paste into which the mercury is introduced according to the first method, consists either of moistened hydrate of strontia or of chloride of strontium. (H. Davy.) Hare proceeds as with barium. (For Clarke's method with the oxy-hydrogen blowpipe, *vid. Schw.* 18, 249, and *Gilb.* 62, 368.)

*Properties.* Of a similar colour to barium, but with less lustre; sinks in oil of vitriol; ductile; less fusible than barium (H. Davy); silver-white (Clarke).

## *Compounds of Strontium.*

### Strontium and Oxygen.

### A. Strontia. SrO.

*Oxide of Strontium, Strontian, Strontit, Strontianerde, Strontiane.*

*Formation.* Strontium oxidizes rapidly (slowly, Clarke) in the air, becoming changed into strontia [or the hydrate ?]. When heated in the air it takes fire and burns, leaving strontia; thrown on water it produces strontia-water, with evolution of hydrogen gas. (H. Davy.)

*Preparation.* By the same methods as those given for baryta; according to Smith, also, by strongly igniting the hydrate.

*Properties.* Greyish-white porous mass, having a specific gravity between 3·0 and 4·0 (H. Davy) = 3·9321. (Karsten.) Not fusing in the fire; not volatile; having an alkaline taste, and an alkaline reaction on vegetable colours; less caustic than potash, soda, or baryta.

| | Calculation. | | Stromeyer. | H. Davy. | Berzelius. |
|---|---|---|---|---|---|
| Sr | 44 | 84·6 | 84·67 | 86 | 84·55 |
| O | 8 | 15·4 | 15·33 | 14 | 15·45 |
| SrO | 52 | 100·0 | 100·00 | 100 | 100·00 |

SrO = 547·29 + 100 = 647·29. (Berzelius.)

*Decomposition.* By electricity, and by the oxy-hydrogen blowpipe.

*Combinations.* *α.* With water. *a.* Hydrate of Strontia.—1. Strontia when mixed with water, crumbles to a white powder and becomes heated.—2. When the crystals of strontia are heated to low redness, the melted hydrate remains as a clear mobile fluid, which solidifies to a greyish-white fibrous mass. (Bucholz, *N. Gehl.* 4, 661.)—3. The crystals of strontia heated to 100°, leave the hydrate in the form of a white powder. (Smith.) By prolonged ignition, the hydrate is rendered transparent (Bucholz); and at a higher temperature, it loses the whole of its water. (Denham Smith, *Phil. Mag. J.* 9, 87; also *Pogg.* 39, 196.)

| | Calculation. | | Smith, No. 3. |
|---|---|---|---|
| SrO | 52 | 85·24 | 85·09 |
| HO | 9 | 14·76 | 14·91 |
| SrO,HO | 61 | 100·00 | 100·00 |

*β.* Crystals of Strontia. Formed during the cooling of a solution of strontia prepared at a higher temperature. Transparent. Crystalline system, the square prismatic (*Fig.* 33); cleaving readily parallel to *p*; less easily, parallel to *r*; $p : e = 137° 48'$; $a : r = 132° 12'$. (Brooke, *Ann. Phil.* 23, 287.) The crystals, when heated (even to 100°, *Smith*) lose 50 per cent. of water, without melting in their water of crystallization,

and leave an effloresced mass of hydrate. (Bucholz.) By exposure to the air they are converted into carbonate of strontia. Sp. gr. = 1·911. (Filhol.)

| | Calculation. | | Smith. | Noad. | R. Phillips. |
|---|---|---|---|---|---|
| SrO | 52 | 39·1 | 39·58 | 38·53 | 36·24 |
| 9HO | 81 | 60·9 | 60·42 | 61·47 | 63·76 |
| SrO,9HO | 133 | 100·0 | 100·00 | 100·00 | 100·00 |

Phillips (*Phil. Mag. J.* 6, 35) supposes the crystals to contain 10 atoms of water. Noad (*Phil. Mag. J.* 11, 301; 12, 52) attributes the excess of water over 9 atoms, which he found, to the mother-liquor adhering to the crystals. Filhol found 9 atoms of water (*J. Pharm. & Chim.* 3, 7, 271).

γ. Strontia-Water. One part of the crystals dissolves in 50 parts of cold, and in 2·4 parts of boiling water. (Bucholz.) Colourless liquid, having an alkaline taste and reaction; becomes covered with a film of carbonate of strontia on exposure to the air; precipitated by sulphuric acid.

*b.* With acids strontia forms the Strontia salts. The specific gravity of these salts lies between that of the baryta and lime salts. They are colourless, when the acid itself is without colour; and not poisonous, unless the acid is so. They colour the blowpipe flame carmine-red; the soluble salts, especially the chloride of strontium, impart this colour also to the flame of a taper, when put upon the wick—to the flame of heated alcohol—and with great vividness, according to Smith, to that of wood-spirit. The similarity of this red colour to that produced by the salts of lithia disappears if a prism is placed between the flame and the eye: in this case, the lithia flame shows only a simple red ray; the strontia flame, on the contrary, exhibits a great number of red rays separated by dark intervals, besides an orange-yellow and a bright blue ray. (Talbot, *Pogg.* 31, 592.)—Hydrochlorate, of strontia, heated on a platinum wire, reddens the blowpipe flame only till it fuses and is converted into chloride of strontium; whereas chloride of lithium reddens it continuously. Chloride of barium mixed with the chloride of strontium prevents the appearance of the red colour with the blowpipe. The colour imparted to the flame of alcohol by chloride of strontium becomes yellowish-red when salts of baryta are present, and yellow when soda salts are present in large quantity. (H. Rose.) Potash and soda withdraw the acid from all salts of strontia, excepting the phosphate and sulphate. Many of the strontia-salts are insoluble in water; but all except the sulphate are dissolved by weak nitric or hydrochloric acid, being at the same time partly decomposed. These salts dissolved in water give a white precipitate, soluble in hydrochloric acid, with the simple carbonate, diphosphate, or arseniate, and with the simple oxalate or tartrate of ammonia, potash, or soda. Bicarbonate of potash precipitates a strontia solution more slowly and less copiously the more it is diluted; and a very dilute solution, only with the aid of heat. Iodate of soda gives a white precipitate with the salts of strontia, immediately in concentrated solutions, but not till after some time when weaker solutions are employed. (H. Rose.) Liebig found no precipitate produced by this reagent—probably because he used a very dilute solution. With simple chromate of potash, the strontia salts give a yellow crystalline precipitate, after some time. With very dilute solutions, *no* precipitate is produced. (Smith.) Sul-

phuric acid and its salts, not excepting a solution of gypsum, precipitate the salts of strontia, even when largely diluted; though not at so great a degree of dilution or so instantaneously as the salts of baryta; the precipitated sulphate of strontia is but slightly soluble in hydrochloric or nitric acid. A solution of nitrate of strontia which contains but one part of strontia in 2,500 parts of water, still gives a precipitate with sulphuric acid or sulphate of soda; with 5,000 parts of water, a slight cloudiness; with 10,000 parts of water, a very slight turbidity; with 20,000 parts of water, a very slight cloudiness after some minutes only; and with 40,000 parts of water, after some minutes, a scarcely perceptible turbidity. With oxalate of ammonia, a solution containing 1 part of strontia in 10,000 parts of water gives a scarcely apparent turbidity; and with more water, no effect whatever. (Lassaigne, *J. Chim. Med.* 8, 527.) Oxalic acid gives a white precipitate which does not appear for some time when the solution is considerably diluted; more rapidly, however, than with a salt of baryta. No precipitate is produced with strontia salts by the following substances: perchloric acid; hydrofluosilicic acid (not, at least, if the solution contains any free acid); bicarbonate of potash; bichromate of potash; hydrosulphate of ammonia; succinate of ammonia (with very concentrated solutions only, a precipitate soluble in hydrochloric acid is formed after a long time); ferrocyanide of potassium (H. Rose, *Pogg.* 44, 445); ferridcyanide of potassium.

c. With earths, forming enamels and glasses.

d. With certain oxides of the heavy metals in the wet way.

e. With certain organic substances.

### B. Peroxide of Strontium.

Not yet known in the separate state, but only as a *Hydrate*, which falls down in pearly scales on mixing strontia-water with an aqueous solution of peroxide of hydrogen, or with the hydrochlorate or nitrate of peroxide of hydrogen, not in excess. (Thénard, *Ann. Chim. Phys.* 8, 313.)

### Strontium and Carbon.

Carbonate of Strontia.—*a. Monocarbonate.*—Found as *Strontianite.* Formed by exposing strontia and its combinations with water to the air. Prepared in the same manner as the carbonate of baryta. May be obtained, according to Zoega, in crystals like those of carbonate of baryta (III., 139).

The crystals of the native carbonate belong to the right prismatic system, and have the forms of arragonite (Fuchs, Mitscherlich); the rhombohedral system (Hauy). It is transparent, has a waxy lustre, and a specific gravity of 3·605 (Mohs); 3·6245 (Karsten). The artificial carbonate is a white substance, smooth to the touch, and has but little cohesion. Fuses at 226° (Wedgwood) to a clear glass. (Saussure, *J. Phys.* 45, 24.) Tasteless. The native variety however has an alkaline reaction. (Pleischl.)

| | Calculation. | | Stromeyer. | Thomson. | Ure. | Schaffgotsch. | Bérard. |
|---|---|---|---|---|---|---|---|
| SrO..... | 52 | 70·27 | .... 70·313 | .... 70·1 | .... 69·8 | .... 69·73 | .... 73·6 |
| $CO^2$..... | 22 | 29·73 | .... 29·687 | .... 29·9 | .... 30·2 | .... 30·27 | .... 26·4 |
| *SrO, $CO^2$* | *74* | *100·00* | .... 100·000 | .... 100·0 | .... 100·0 | .... 100·00 | .... 100·0 |

| | Klaproth, Kirwan. | | Pelletier. | | Hope. |
|---|---|---|---|---|---|
| SrO ..... | 69·5 | .... | 62 | .... | 61·2 |
| $CO^2$ ..... | 30·0 | .... | 30 | .... | 30·2 |
| Water ..... | 0·5 | .... | 8 | .... | 8·6 |
| | 100·0 | .... | 100 | .... | 100·0 |

It volatilizes with a red light when heated on a piece of charcoal inflamed by a stream of oxygen gas. It loses carbonic acid if exposed to the heat of a powerful forge. (Gay-Lussac & Thénard.) The change is complete in three-quarters of an hour, the substance retaining its form but diminishing in volume. (Abich. *Pogg.* 23, 315.) It loses its acid at a lower temperature if steam is passed over it, the hydrate being then produced. (Gay-Lussac & Thénard.) Before the blowpipe it fuses at the edges, and then rapidly swells up, forming cauliflower-like ramifications, which become highly incandescent, impart a reddish colour to the flame, and have an alkaline reaction. (Berzelius.) It is readily dissolved by a cold solution of hydrochlorate, nitrate, or succinate of ammonia. (A. Vogel, Brett, Wittstein.) 74 parts (1 At.) of carbonate of strontia boiled for eight hours with a solution of 54 parts (1 At.) of sal-ammoniac in water, dissolve all but 3·3 parts with evolution of carbonate of ammonia; the whole of the ammonia is evolved. (Smith.) Carbonate of strontia is soluble in 1536 parts of boiling water. (Hope.) ¶ Also in 11,862 parts of water acidulated with hydrochloric or sulphuric acid, and in 18,045 parts of pure water at ordinary temperatures. (Fresenius.) ¶

*b. Acid Salt.*—The salt *a* is slightly soluble in aqueous carbonic acid, and again separates in needles when the liquid is evaporated. The solution exerts an alkaline reaction on the blue colour of violets and on reddened litmus. (Pleischl.)

### Strontium and Boron.

Borate of Strontia.—*a. Biborate.*—By precipitating a neutral salt of strontia with borax.—White powder, colouring the juice of violets green; soluble in 130 parts of boiling water. (Hope.) It dissolves readily in a cold aqueous solution of hydrochlorate or nitrate of ammonia. (Brett.)

*b. Sexborate.*—The white precipitate produced in a salt of strontia by the addition of sexborate of potash. It is soluble in a large quantity of water, and has an alkaline reaction. (Laurent.)

### Strontium and Phosphorus.

A. Phosphide of Strontium.—Similar in properties to phosphide of barium.

B. Hypophosphite of Strontia.—Obtained as the baryta salt, according to the first and second methods (III., 141). Difficultly crystallizable. (Dulong.) Very similar to the baryta salt. Like that salt it evolves, when heated, spontaneously inflammable phosphuretted hydrogen gas, attended with the same phenomena, and leaves diphosphate of strontia mixed with phosphoric oxide. (H. Rose, *Pogg.* 9, 372; 12, 84.) Very soluble in water. *(Dulong.)*

C. Phosphite of Strontia.—*Diphosphite.*—Crystallizes from an aqueous solution by spontaneous evaporation. (Dulong.) Terchloride of phosphorus dissolved in water gives, after being saturated with ammonia, a scanty precipitate with chloride of strontium; but on evaporating the mixture, the salt is deposited in a crystalline form. The salt washed and dried in vacuo over oil of vitriol, and then ignited, evolves hydrogen gas with a trace of water and phosphorus, and leaves di-[pyro-] phosphate of strontia with a small excess of base and a little phosphoric oxide.

$$2SrO, 2HO, PO^3 = 2SrO, PO^5 + 2H.$$

(H. Rose, *Pogg.* 9, 27.) It dissolves with difficulty in water; the solution when heated deposits a *basic salt* of a pearly lustre [triphosphite ?], whilst an *acid salt* [monophosphite ?], which crystallizes with difficulty, remains dissolved. (Dulong.)

D. Phosphate of Strontia.—*Diphosphate.*—Formed when chloride of strontium or nitrate of strontia is precipitated by ordinary diphosphate of soda. White, tasteless powder, which melts before the blowpipe to a white enamel. (Vauquelin.) Not decomposed by potash or soda. (Berzelius.) Does not dissolve in water, but is soluble in aqueous phosphoric, hydrochloric, or nitric acid. (Vauquelin.) Easily soluble in a cold solution of hydrochlorate, nitrate, or succinate of ammonia, from which it is partly precipitated by a small quantity of ammonia, and completely by a larger quantity. (Brett, Wittstein.)

| | After ignition. | | Vauquelin. | Stromeyer. |
|---|---|---|---|---|
| 2SrO | 104·0 | 59·29 | 58·76 | 63·435 |
| $PO^5$ | 71·4 | 40·71 | 41·24 | 36·565 |
| 2SrO, $PO^5$ | 175·4 | 100·00 | 100·00 | 100·000 |

¶—E. Pyrophosphate of Strontia.—Nitrate of strontia gives a white amorphous precipitate with pyrophosphate of soda. If, however, the mixture be heated, the amorphous powder is converted into small crystals. Somewhat soluble in water; dissolves completely in nitric and hydrochloric acid; insoluble in acetic acid and solution of pyrophosphate of soda. The salt contains water.

| | Calculation. | | Schwarzenberg. |
|---|---|---|---|
| 2SrO | 104·0 | 59·22 | 59·19 |
| $PO^5$ | 71·4 | 40·78 | 40·71 |
| 2SrO, $PO^5$ | 175·4 | 100·00 | 99·90 |

(Schwarzenberg, *Ann. Pharm.* 65, 133.)

F. Metaphosphate of Strontia.—Prepared as the baryta-salt by decomposing carbonate of strontia with dilute phosphoric acid, evaporating to dryness, and heating to 316°. Insoluble in water and acids, but decomposed by sulphuric acid.

| | Calculation. | | Maddrell. |
|---|---|---|---|
| SrO | 52·0 | 28·52 | 28·337 |
| $PO^5$ | 71·4 | 71·48 | 71·663 |
| SrO, $PO^5$ | 123·4 | 100·00 | 100·000 |

*(Maddrell, Mem. Chem. Soc. London*, 3, 273, 1848.) ¶

### Strontium and Sulphur.

A. Monosulphide of Strontium.—100 parts of sulphate of strontia strongly ignited in a charcoal crucible yield 64 parts of sulphide of strontium. This substance is white, granular, caked together, but friable. (Berthier.) Sulphate of strontia is more easily decomposed by charcoal than sulphate of baryta. In preparing sulphide of strontium, for the purpose of obtaining the different salts of strontia from it, the methods given for the preparation of sulphide of barium may be employed, especially *a*, *α* and *β* (III. 146). The charcoal should, however, amount to about one-third of the sulphate of strontia.

| | Calculation. | | Berthier. |
|---|---|---|---|
| Sr | 44 | 73·33 | 73·17 |
| S | 16 | 26·67 | 26·83 |
| SrS | 60 | 100·00 | 100·00 |

A solution of sulphide of strontium in boiling water deposits, on cooling, a considerable quantity of crystals of pure strontia. (Berthollet, *J. Polytechn. Cah.* 11, 315; H. Rose, *Pogg.* 55, 430.) The mother-liquor contains double sulphide of hydrogen and strontium or bihydrosulphate of strontia. If an insufficient quantity of water is used to dissolve out the sulphide of strontium, the water chiefly takes up bihydrosulphate of strontia, and the residue treated with a fresh quantity of water yields nearly pure strontia. (H. Rose.)

B. Sulphide of Hydrogen and Strontium, or Bihydrosulphate of Strontia.—1. Strontia-water, or water in which sulphide of strontium is diffused, is saturated with sulphuretted hydrogen gas. (Berzelius.) 2. Sulphide of strontium is dissolved in boiling water, and the strontia allowed to separate on cooling. (H. Rose.) The liquid obtained by the first method yields, when evaporated in vacuo over oil of vitriol, large striated prisms, which appear to be four-sided, and when dry, do not alter by exposure to the air for several days; when heated, they melt in their own water of crystallization—give up this water, together with the second atom of sulphuretted hydrogen, with ebullition—and leave monosulphide of strontium in the form of a white powder. (Berzelius, *Pogg.* 6, 442.) The aqueous solution boiled in a retort evolves sulphuretted hydrogen gas abundantly,—even more readily than the baryta compound; and on cooling, deposits crystals of strontia, with which, when the liquid becomes highly concentrated, crystals of bihydrosulphate of strontia are mixed. (Berthollet, H. Rose.)

C. Persulphide of Strontium.—Similar in character to the persulphide of barium.

D. Hyposulphite of Strontia. Formed when a solution of sulphide of strontium is exposed to the air, or sulphurous acid is passed through it, till it becomes colourless. (Herschel.) In the first case, carbonate of strontia is precipitated; in the second, sulphur. On mixing the liquid with alcohol, the hyposulphite of strontia separates in delicate, silky crystals. (Grotthuss, *Schw.* 9, 334.) By evaporation, the salt is obtained in transparent, rhomboidal crystals. (*Gay-Lussac.*) The crystals are very large, (Rammels-

berg.) The salt tastes insipid at first, and sulphurous afterwards; it is neutral to vegetable colours. (Gay-Lussac.) Permanent in the air. Loses its water between 50° and 60°, without however suffering decomposition. At a higher temperature, it is converted into sulphate of strontia and sulphide of strontium, with separation of sulphur. (Gay-Lussac.) Does not part with its water at 60°, and still retains 6 per cent. of water at 180°. By a somewhat stronger heat it is resolved into water, sulphur, and a small quantity of sulphurous acid, which escape, and a white pulverulent residue composed of sulphide of strontium with sulphite and sulphate of strontia. (Rammelsberg, *Pogg.* 56, 301.) Treated with nitric acid, it is converted into sulphate of strontia containing a double quantity of sulphuric acid. (Gay-Lussac, *Ann. Chim.* 85, 199; 95, 165.) It dissolves in 6 parts of cold water (Gay-Lussac); in 4 parts of water at 13°; and in $1\frac{1}{4}$ parts of boiling water. (Herschel.)

| | Crystallized. | | | Rammelsberg. |
|---|---|---|---|---|
| SrO | 52 | .... | 35·86 | 36·09 |
| $S^2O^2$ | 48 | .... | 33·10 | |
| 5HO | 45 | .... | 31·04 | |
| SrO, $S^2O^2$ + 5Aq. | 145 | .... | 100·00 | |

¶—E. Tetrathionate of Strontia.—SrO, $S^4O^5$ + 6Aq. Obtained in the same manner as the baryta-salt, but less completely precipitated by alcohol. (Kessler, *Pogg.* 74, 249.) ¶

F. Sulphite of Strontia.—Tasteless powder, scarcely soluble in water; changing into sulphate of strontia when exposed to the air.

G. Hyposulphate of Strontia.—Belongs to the rhombohedral system of crystallization (*Fig.* 132); indistinct cleavage-plane parallel to $p$; $r : r^3 = 120°$. Taste, bitter. Permanent in the air; decrepitates slightly in the fire; and leaves, after ignition, 57·75 per cent. of sulphate of strontia. Dissolves in 4·5 parts of water at 16°; in 1·5 parts of boiling water, but not in alcohol. (Heeren.)

| | Crystallized. | | | Heeren. |
|---|---|---|---|---|
| SrO | 52 | .... | 32·5 | 32·54 |
| $S^2O^5$ | 72 | .... | 45·0 | 45·36 |
| 4HO | 36 | .... | 22·5 | 22·10 |
| SrO, $S^2O^5$ + 4Aq. | 160 | .... | 100·0 | 100·00 |

H. Sulphate of Strontia.—*a. Monosulphate.*—Found in nature as *Cœlestine*. Precipitated on mixing a salt of strontia in solution with sulphuric acid, or a soluble sulphate. A solution of gypsum also precipitates the strontia salts. Strontia becomes heated on the addition of oil of vitriol, without however rising to a red heat. (Jul. Fontenelle & Quesneville, *Ann. Chim. Phys.* 37, 223.) By using large quantities, a red heat is produced. (Kastner, *Kastn. Arch.* 16, 229.)

The native sulphate belongs to the right prismatic system of crystallization (*Fig.* 61, and many other forms); cleavage parallel to $p$, and less easy in the direction of $u$ and $u^1$; $u^1 : u = 104° 48'$ (Hauy), 103° 42′ (Phillips). Specific gravity of the native sulphate = 3·953 (Breithaupt), that of the artificial = 3·5883. (Karsten.) The artificially prepared salt has the form of a white powder. It is tasteless; at a high temperature it fuses to a vitrefied mass.

| | Calculation. | | Stromeyer. | Kirwan, Clayfield, Henry, Klaproth. | Vauquelin. |
|---|---|---|---|---|---|
| SrO | 52 | 56·52 | 57 | 58 | 54 |
| $SO^3$ | 40 | 43·48 | 43 | 42 | 46 |
| SrO, $SO^3$ | 92 | 100·00 | 100 | 100 | 100 |

By ignition with charcoal it is reduced to sulphide of strontium. According to Moretti (*Schw.* 9, 169) arsenic acid with the aid of heat expels the sulphuric acid. It dissolves in 3,840 parts of boiling water (Hope); in 15,029 parts of water at 11°; in 3,544 parts of boiling water (Brandes & Silber, *Br. Arch.* 33, 61); in 3,600 parts of water at 15·5°; in 6,895 parts of water at 14°, and in 9,638 parts of boiling water (Fresenius);—less freely in water containing sulphate of soda, and still less in water mixed with sulphuric acid (Andrews, *Phil. Mag. Ann.* 7, 406). It dissolves slowly, but completely, in a solution of common salt (by which character it is distinguished from sulphate of baryta), and is again precipitated by sulphuric acid. (Wackenroder.) Insoluble in solution of sal-ammoniac. (Brett.)

*b. Acid Salt.*—The neutral sulphate of strontia is taken up by boiling oil of vitriol, from which it is again thrown down by water. (Hope, Klaproth, Moretti.)

I. Sulphide of Carbon and Strontium and Hydrosulpho-carbonate of Strontia.—The brownish-yellow solution evaporated in vacuo leaves a fibrous, pale, lemon-coloured, effloresced mass, which becomes reddish brown when moistened, and is more soluble in water than the baryta-salt. (Berzelius.)

## Strontium and Selenium.

A. Monoselenide of Strontium and Hydroseleniate of Strontia.—Soluble.

B. Polyselenide of Strontium and Hydroselenite of Strontia.—Hydroselenite of potash produces with strontia-salts a flesh-coloured precipitate, which does not lose selenium at a red heat; acids however separate selenium from it. (Berzelius.)

C. Selenite of Strontia.—*a. Monoselenite.*—$SeO^2$, SrO.—White infusible powder, insoluble in water.

*b. Biselenite.*—Obtained in the same manner as the biselenite of baryta. It separates as a milk-white, amorphous crust on evaporating an aqueous solution. Fuses in the fire; swells up and evolves water at first, and then one half of its acid, leaving a spongy residue of monoselenite of strontia. Scarcely soluble in cold water, and dissolved but slowly even by boiling water. (Berzelius.)

## Strontium and Iodine.

A. Iodide of Strontium.—Prepared by saturating aqueous hydriodic acid with strontia, carbonate of strontia, or sulphide of strontium, and evaporating; or by the method of O. Henry given under iodide of barium

(III., 154). Fuses in a close vessel below a red heat without undergoing decomposition; but if heated in the air it gives off iodine and is converted into strontia. Readily dissolved by water. (Gay-Lussac.)

*Iodide of Strontia?*—Iodine combines with strontia at a red heat. (Gay-Lussac.) The compound contains equal numbers of atoms of iodine and strontia, and loses its iodine if the heat be too powerful. (Grouvelle.)

B. Iodate of Strontia.—1. Formed by dissolving iodine in strontia-water; most of the iodate of strontia falls down, whilst the iodide of strontium remains in solution. (Gay-Lussac.)—2. By precipitating an aqueous solution of chloride of strontium with iodate of soda.—*a*. If the liquids are used hot, the salt $\alpha$ is obtained in the state of powder;—*b*. In the cold, the salt $\beta$ is obtained in crystals. (Rammelsberg, *Pogg.* 44, 575.) The anhydrous salt when ignited evolves vapour of iodine and 12·452 per cent of oxygen gas, leaving a residue of 40·244 per cent. of five-basic periodate of strontia.

$$5(SrO, IO^5) = 5SrO, IO^7 + 4I + 18\,O.$$

It dissolves easily in cold hydrochloric acid, the liquid acquiring a dark yellow colour and evolving chlorine. (Rammelsberg.)

$\alpha$. *With one atom of water.*—Method 2, *a*. White powder.

$\beta$. *With 6 atoms of water.*—Method 1, or 2, *b*. Small crystals, which appear to be octohedrons. (Gay-Lussac.)

One part of salt $\beta$ dissolves in 416 parts of water at 15°, and in 138 parts of boiling water. (Gay-Lussac.) It dissolves in 342 parts of water at 15°, in 110 parts of boiling water, and also in warm nitric acid, but with difficulty. (Rammelsberg.)

| | Anhydrous. | | | | Salt $\alpha$. | | | Rammelsberg. |
|---|---|---|---|---|---|---|---|---|
| SrO | 52·0 | .... | 23·85 | SrO | 52 | .... | 22·91 | .... 23·37 |
| $IO^5$ | 166·0 | .... | 76·15 | $IO^5$ | 166 | .... | 73·13 | .... 72·46 |
| | | | | HO | 9 | .... | 3·96 | .... 4·17 |
| $SrO, IO^5$ | 218·0 | .... | 100·00 | + Aq. | 227 | .... | 100·00 | .... 100·00 |

| | Salt $\beta$. | | | Rammelsberg. |
|---|---|---|---|---|
| SrO | 52 | .... | 19·12 } | ..... 79·86 |
| $IO^5$ | 166 | .... | 61·03 } | |
| 6HO | 54 | .... | 19·85 | ..... 20·14 |
| + 6Aq. | 272 | .... | 100·00 | ..... 100·00 |

C. Five-basic Periodate of Strontia.—Remains after the ignition of iodate of strontia. Gives the same appearances when heated in hydrogen gas as the baryta-salt, but with less vivid incandescence. (Rammelsberg.)

## Strontium and Bromine.

A. Bromide of Strontium.—The solution of carbonate of strontia in aqueous hydrobromic acid is evaporated to dryness and exposed to heat. White mass, fusing at a red heat without decomposition. (Berthemot, Rammelsberg.)

*Sex-hydrated Bromide of Strontium*, or *Penta-hydrated Hydrobromate of Strontia.* Crystallizes on evaporating and cooling an aqueous solution of the bromide of strontium.—Very long needles. (Löwig, *Mag. Pharm. 33, 7.)* According to Berthemot (*Ann. Chim. Phys.* 74, 394), they

effloresce in the air; according to Rammelsberg (*Pogg.* 55, 238), they do not effloresce even over oil of vitriol. The crystals become anhydrous when gently heated (Löwig), but first melt in their water of crystallization. (Rammelsberg.) They communicate a purple-red colour to the flame of alcohol or of a taper. (Löwig.)

| Anhydrous. | | | | Hydrated. | | | | Rammelsberg. |
|---|---|---|---|---|---|---|---|---|
| Sr | 44·0 | 35·95 | | Sr | 44·0 | 24·94 | 69·76 | |
| Br | 78·4 | 64·05 | | Br | 78·4 | 44·45 | | |
| | | | | 6HO | 54·0 | 30·61 | | 30·24 |
| Sr, Br | 122·4 | 100·00 | | | 176·4 | 100·00 | | 100·00 |

Or:

| | | |
|---|---|---|
| SrO | 52·0 | 29·48 |
| HBr | 79·4 | 45·01 |
| 5HO | 45·0 | 25·51 |
| | 176·4 | 100·00 |

B. Hypobromite of Strontia?—Bromine behaves with strontia-water as with baryta-water (III., 156), excepting that no bromate of strontia is precipitated. (Balard.)

C. Bromate of Strontia.—1. A solution of carbonate of strontia in aqueous bromic acid is evaporated to the crystallizing point. (Rammelsberg, *Pogg.* 52, 84 and 87.)—2. Crystals of strontia and bromine are stirred up in water till they dissolve, and the solution is evaporated at a gentle heat. The bromate of strontia crystallizes rather before the hydrated bromide of strontium; but the two compounds cannot be completely separated by re-crystallization. (Löwig, *Mag. Pharm.* 33, 7.)—By warming the crystals the dry salt is obtained; it is decomposed at a red heat into oxygen gas and bromide of strontium. (Löwig.) In this respect it behaves like the baryta-salt, though the decomposition is not so violent. (Rammelsberg.)

The crystals contain one atom of water. Crystalline system, the right prismatic. Right rhombic prisms. (*Fig.* 69.) $u^1 : u = 98^\circ\ 40'$; $i : i^1 = 78^\circ\ 15'$. They do not lose their water when placed over oil of vitriol in vacuo at ordinary temperatures; but are rendered completely anhydrous at a temperature of 120°. (Rammelsberg.) According to Löwig, the salt forms four-sided needles, more solid and less transparent than the hydrated bromide of strontium; effloresing in dry air. The crystals dissolve in 3 parts of cold water. (Rammelsberg.)

| Anhydrous. | | | | Crystallized. | | | Rammelsberg. |
|---|---|---|---|---|---|---|---|
| SrO | 52·0 | 30·52 | | SrO | 52·0 | 28·99 | 28·82 |
| $BrO^5$ | 118·4 | 69·48 | | $BrO^5$ | 118·4 | 66·00 | 66·19 |
| | | | | HO | 9·0 | 5·01 | 4·99 |
| $SrO, BrO^5$ | 170·4 | 100·00 | | $SrO, BrO^5 + Aq.$ | 179·4 | 100·00 | 100·00 |

## Strontium and Chlorine.

A. Chloride of Strontium.—Strontia heated in chlorine gas is converted into chloride of strontium, with separation of half a volume of oxygen gas for every measure of chlorine gas absorbed. Strontia when hot, absorbs hydrochloric acid gas, with incandescence and formation of

water. (Chevreul.) The chloride is obtained in the anhydrous state by igniting the hydrated compound. When moderately heated, it forms a white powder; after fusion, a white, semi-transparent, vitrefied mass. It is difficult to fuse; permanent in the fire; a non-conductor of electricity; of a sharp bitter taste; of specific gravity about 2·8033. (Karsten.) When ignited in the air, it becomes alkaline from loss of chlorine and absorption of oxygen. (Kraus, *Pogg.* 43, 139.) This is an instance of reciprocal affinity. Dissolves in 116·4 parts of alcohol, containing 99·3 per cent., and in 262 parts at a boiling temperature. (Fresenius.)

| | Calculation. | | H. Davy. |
|---|---|---|---|
| Sr | 44·0 | 55·4 | 58 |
| Cl | 35·4 | 44·6 | 42 |
| SrCl | 79·4 | 100·0 | 100 |

| Or: | Calculation. | | Vauquelin. | Val. Rose. | Stromeyer. | Kirwan. |
|---|---|---|---|---|---|---|
| SrO | 52·0 | 65·5 | 60·7 | 61·67 | 65·585 | 69 |
| $MuO^2$ | 27·4 | 34·5 | 39·3 | 38·33 | 34·415 | 31 |
| SrO, $MuO^2$ | 79·4 | 100·0 | 100·0 | 100·00 | 100·000 | 100 |

*Sex-hydrated Chloride of Strontium*, or *Penta-hydrated Hydrochlorate of Strontia.* Chloride of strontium unites with water, with evolution of heat.—*Preparation.* Similar to that of hydrochlorate of baryta (III. 158). The simplest method is to dissolve in water the sulphide of strontium, obtained by igniting cœlestine with $\frac{1}{3}$ its weight of charcoal, and saturate the filtrate with hydrochloric acid. Long six-sided needles, imparting a peculiarly intense red colour to the flame of alcohol or of a taper. When heated, they fuse and are converted into dry chloride of strontium. They deliquesce only in moist air; dissolve in $\frac{2}{3}$ pt. of cold water; and in hot water in every proportion. Concentrated hydrochloric acid throws down part of the salt from its solution in water. (Hope.) The crystals dissolve at 15° in 6 parts of alcohol of specific gravity 0·833 (Vauquelin); in 24 parts of cold, and in 19 parts of boiling absolute alcohol. (Bucholz.)

| | Calculation. | | Kirwan. | Vauquelin. |
|---|---|---|---|---|
| SrCl | 79·4 | 59·52 | 58 | 60 |
| 6HO | 54·0 | 40·48 | 42 | 40 |
| SrCl, 6Aq. | 133·4 | 100·00 | 100 | 100 |

| Or: | | |
|---|---|---|
| SrO, HCl | 88·4 | 66·27 |
| 5HO | 45·0 | 33·73 |
| SrO, HCl + 5Aq. | 133·4 | 100·00 |

¶ B. Chlorite of Strontia.—Prepared in the same manner as the baryta-salt. Less easily decomposed by slow evaporation; deliquescent; decomposed at 208° into chlorate and chloride. (Mitton.) ¶

| | Calculation. | | Millon. |
|---|---|---|---|
| SrO | 52·0 | 46·32 | 46·47 |
| $ClO^3$ | 59·4 | 53·68 | 53·53 |
| SrO, $ClO^3$ | 111·4 | 100·00 | 100·00 |

C. Chlorate of Strontia.—Obtained in the same manner as the *chlorate of baryta*. Crystallizes in needles (large pyramidal crystals,

*Wächter*); tastes cooling, sharp, and somewhat rough. Contains, according to Chenevix, 26 per cent. of strontia, 46 of chloric acid, and 28 of water. Fuses and explodes with a purple flame on ignited charcoal. (Vauquelin.) Decomposed at the same temperature as the baryta-salt. (Wächter.) Deliquesces in the air, and dissolves in alcohol more readily than the hydrochlorate of strontia. (Chenevix.)

D. PERCHLORATE OF STRONTIA.—The solution evaporated to the consistence of syrup solidifies on cooling to a mass of crystals, which, however, rapidly deliquesce even in the drying chamber. A solution of the salt in alcohol burns with a splendid purple flame. (Serullas, *Ann. Chim. Phys.* 46, 304.)

## STRONTIUM AND FLUORINE.

FLUORIDE OF STRONTIUM.—Prepared in the same manner as the fluoride of barium. White powder. Dissolves but very slightly in water and in aqueous hydrofluoric acid. (Berzelius, *Pogg.* 1, 20.)

## STRONTIUM AND NITROGEN.

A. NITRITE OF STRONTIA.—Crystallizes in fan-shaped masses of needles which slowly deliquesce in the air. (Fischer, *Pogg.* 74, 115.) The crystals are permanent in the air. (Mitscherlich.)

B. NITRATE OF STRONTIA.—Prepared by the same methods as the nitrate of baryta. Separates in anhydrous crystals from an aqueous solution concentrated by heat; when it is exposed in a more dilute state to a low temperature, hydrated crystals are produced.

The anhydrous salt forms transparent and colourless octohedrons and cubo-octohedrons (*Figs.* 2 and 4); it has a sharp cooling taste, decrepitates in the fire, and fuses at a red heat, undergoing decomposition and leaving strontia. Explodes but slightly on ignited charcoal, and with a red flame.

| | Anhydrous. | | | Stromeyer. | Cooper. | Richter. |
|---|---|---|---|---|---|---|
| SrO | 52 | .... | 49 | 49·38 | 49·08 | 48·6 |
| $NO^5$ | 54 | .... | 51 | 50·62 | 50·92 | 51·4 |
| SrO, $NO^5$ | 106 | .... | 100 | 100·00 | 100·00 | 100·0 |

The *hydrated salt* belongs to the oblique prismatic system; (*Fig.* 107), but without the *t*-face, and consequently with the *f*-face; $p : u = 103° 40'$; $p : f$ *backwards* $= 131° 47'$; $u : u^1 = 66° 20'$; $u^1 : m$ (the face to the right of $u^1$) $= 146° 50'$; $u : z = 140° 10'$; $p : z = 111° 5'$; $z^1 : z = 126°$. Highly efflorescent. (Brooke, *Ann. Phil.* 23, 289.)

Nitrate of strontia dissolves in 5 parts of cold and in ½ pt. of boiling water; it is not soluble in absolute alcohol.

| | Hydrated. | | | Cooper. | Kirwan. |
|---|---|---|---|---|---|
| SrO | 52 | .... | 34·44 | 35·4 | 36·21 |
| $NO^5$ | 54 | .... | 35·76 | 36·8 | 31·07 |
| 5HO | 45 | .... | 29·80 | 27·8 | 32·72 |
| SrO, $NO^5$ + 5Aq. | 151 | .... | 100·00 | 100·0 | 100·00 |

C. Ammonio-bromide of Strontium.—Powdered anhydrous bromide of strontium absorbs ammoniacal gas. The compound forms a clear solution in water. (Rammelsberg, *Pogg.* 55, 238.)

| | Calculation. | | Rammelsberg. |
|---|---|---|---|
| $4SrBr$ | 489·6 | 96·65 | 96·8 |
| $NH^3$ | 17·0 | 3·35 | 3·2 |
| $4SrBr, NH^3$ | 506·6 | 100·00 | 100·0 |

D. Ammonio-chloride of Strontium. — Anhydrous chloride of strontium in powder absorbs ammoniacal gas greedily, forming a white, loose, very bulky powder, which gives off the ammonia when heated. (H. Rose, *Pogg.* 20, 155.)

| | Calculation. | | H. Rose. |
|---|---|---|---|
| $SrCl$ | 79·4 | 53·87 | 54·19 |
| $4NH^3$ | 68·0 | 46·13 | 45·81 |
| $SrCl, 4NH^3$ | 147·4 | 100·00 | 100·00 |

## Strontium and Sodium.

74 parts (1 At.) of *carbonate of strontia* fuse with 53·2 parts (1 At.) of dry *carbonate of soda* at a strong red heat, forming a mass which, when cold, exhibits a stony texture, and an uneven, slightly crystalline fracture; it does not give up carbonic acid, even at a white heat. (Berthier, *Ann. Chim. Phys.* 38, 247.) Carbonate of strontia gives with carbonate of soda, on charcoal before the blowpipe, a clear glass, which becomes milk-white when cold (any excess of the carbonate of strontia remains undissolved). If the heat be increased, the compound boils, gives off carbonic acid, and sinks into the charcoal. (Berzelius.)

With *borax* and *microcosmic salt*, strontia behaves like baryta. (Berzelius.)

¶ Baer succeeded in preparing a double pyrophosphate of strontia and soda similar to the baryta-salt (p. 164), but from the formula which he gives—$2SrO, 9PO^5 + NaO, PO^5 + 18$ Aq.—it would appear to be a mere mixture. ¶

92 parts (1 At.) of *sulphate of strontia* yield with 53·2 parts (1 At.) of dry *carbonate of soda*, a very fusible mixture, which is not volatile at a white heat, and when solidified is white, opaque, and stony, with an uneven, very slightly crystalline fracture. (Berthier.)

## Strontium and Strontium.

One atom of *carbonate of strontia* gives with one atom of *chloride of strontium*, at a moderate red heat, a clear, mobile liquid, which solidifies on cooling to a homogeneous, porcelain-like mass, of laminated texture. (Döbereiner, *Pogg.* 15, 240.)

One atom of *sulphate of strontia* fuses readily with one atom of *chloride of strontium:* the solidified mass is homogeneous and translucent, with a crystalline fracture.

Strontium also combines with mercury.

## Chapter VI.

# CALCIUM.

*History.* Lime has been known from the earliest times. Black, in 1756, first pointed out the difference between burnt and unburnt lime. Sir H. Davy discovered calcium in 1808.

*Sources.* Calcium is the most widely diffused of all the alkali-metals; it is found in all three kingdoms, especially as carbonate, phosphate, sulphate, hydrochlorate, nitrate, arseniate, and tungstate of lime; also as silicate of lime, either alone or in combination with other silicates, constituting numerous minerals; lastly, as fluoride of calcium.

*Preparation.* Similar to that of barium according to the first and second methods. (H. Davy, *Gilb.* 32, 369; Berzelius & Pontin, *Gilb.* 36, 255; Gay-Lussac & Thénard, *Recherch.* 1, 50; Hare.) In the first method, however, the separation of the mercury is more difficult.

*Properties.* Silver white; solid at ordinary temperatures.—*Atomic weight of Calcium* = 20·5 (Berzelius), = 20 (Dumas, *Compt. rend.* 14, 546; Erdmann & Marchand, *J. pr. Chem.* 26, 472).

### *Compounds of Calcium.*

### Calcium and Oxygen.

### A. Lime. CaO.

*Oxide of Calcium; Chaux; Terre calcaire; Kalkerde, Kalk.*

*Formation.* The metal oxidizes rapidly in the air at ordinary temperatures; and with inflammation when heated. It dissolves in water, producing lime-water and liberating hydrogen gas. (H. Davy.)

*Preparation.*—By prolonged ignition of carbonate of lime. On the large scale, common lime-stone is burned in lime-kilns; on the small scale, calc-spar, white marble, oyster-shells, or artificially prepared carbonate of lime is ignited in crucibles; the last portions of carbonic acid are got rid of by moistening the substance with water and igniting again. Impure lime-stone containing clay becomes *dead-burnt*, when subjected to too strong a heat,—*i. e.* it is changed into a half-fused compound of lime with silica and alumina, which no longer evolves heat with water, and consequently is but imperfectly slaked by it. Lime of this kind is mentioned by Bergman. (*Opusc.* 1, 27.) Pure carbonate of lime, such as Carrara

marble, does not become *dead-burnt* even in the most powerful forge, or after repeated ignition in a potter's furnace. (Gehlen, *N. Gehl.* 3, 308; Nasse, *Schw.* 46, 91.) Oyster-shells and chalk become *dead-burnt* under certain circumstances. (Bucholz, *N. Gehl.* 4, 128; see also Vicat, *Ann. Chim. Phys.* 23, 424; and *Schw.* 46, 126.)

*Properties.* White, soft, and easily reduced to powder. Specific gravity = 2·3 (Kirwan); = 3·08, at 4°, in vacuo (Royer & Dumas); = 3·1605 (Karsten); = 3·179 (Pol. Boullay); = 3·2 (Richter). Lime is one of the most refractory bodies in nature, melting only with the strongest heat of a powerful voltaic battery (H. Davy), or on charcoal ignited in a stream of oxygen gas (Morveau), or in the flame of the oxy-hydrogen blowpipe (Clarke); in the last case it emits a splendid red light. It fuses to a white, opaque enamel, but generally at the edges only. It is not volatile. Taste, alkaline. Alters vegetable colours like the alkalis. It is the least caustic in its action of all the alkalis.

| | Calculation. | | Berzelius. | Sir H. Davy. | |
|---|---|---|---|---|---|
| | | | | Earlier. | Later. |
| Ca | 20 .... 71·43 | .... | 71·91 .... | 73·5 .... | 72·8 |
| O | 8 .... 28·57 | .... | 28·09 .... | 26·5 .... | 27·2 |
| CaO | 28 .... 100·00 | .... | 100·00 .... | 100·0 .... | 100·0 |

(CaO = 256·02 + 100 = 356·02. Berzelius.)

*Decomposition.* By electricity; by potassium at a white heat; by phosphorus, sulphur, bisulphide of carbon (II., 204, 3), and chlorine at a red heat.

*Combinations.—a.* With water.

*a.* Hydrate of Lime.—*Slaked Lime.* Lime mixed with about half its weight of water, absorbs it at first by capillary attraction into the pores left in its substance by the escape of carbonic acid during the process of burning. The air contained in the pores is thus driven out with a hissing noise, and the lime combines with the water, forming a pulverulent hydrate. The combination is attended with great rise of temperature—sometimes even sufficient to inflame sulphur, gunpowder (*Ann. Chim. Phys.* 23, 217), and wood—and more sudden and powerful in proportion to the purity of the lime and the quantity employed. Even with ice, lime becomes heated to a temperature of 100°. The steam, as it rises, carries with it a large quantity of lime. When lime is moistened with a small quantity of water, it emits while slaking, a bright light visible in the dark. (Pelletier, Kortüm, Voight, *N. Mag.* 2, 69; Heinrich, *Phosphorescenz*, 573; Göbel, *Schw.* 58, 488.) Lime on which a treble quantity of water is poured crumbles, with violent ebullition, to a cream-like mixture of hydrate of lime and lime-water. The production of heat during the slaking cannot by any means be referred to the mere passage of the water from the liquid to the solid state, since ice evolves heat with lime. The statement of Grotthus, that ammonia is evolved in the slaking of lime, has been refuted by Pleischl. (*Zeitschr Phys.Math.* 2, 315.) Lime exposed to the air is converted into a compound of hydrate of lime with carbonate (III., 188).

Hydrate of lime is obtained in the crystalline state, either, according to Chompré & Riffault (*Gilb.* 28, 117), by bringing two cups connected by means of asbestos into the circuit of a voltaic battery,—the positive cup containing nitrate of lime, and the negative cup water,—whereupon the

crystals of lime are deposited on the wire of the negative cup; or more readily, according to Gay-Lussac (*Ann. Chim. Phys.* 1, 334), by placing a vessel containing lime-water and another containing oil of vitriol under a glass jar, closed at bottom, the oil of vitriol being renewed as often as it becomes saturated with water.

The hydrate obtained by slaking lime has the form of a fine white powder; the crystallized hydrate forms transparent, regular, six-sided prisms, perpendicularly truncated, and cleaving parallel to the terminal faces; also six-sided tables, often cleaving in planes parallel to the lateral faces of a rhomboid. (Gay-Lussac.) It loses its water at a low red heat, but without fusing. In the air it absorbs carbonic acid, by which the crystals are rendered opaque.

| | Calculation. | | Dalton. | Berzelius. | Gay-Lussac. Crystals. | Lavoisier. |
|---|---|---|---|---|---|---|
| CaO ..... | 28 | 75·67 | 75 | 75·7 to 75·5 | 76·25 | 77·7 |
| HO..... | 9 | 24·33 | 25 | 24·3 „ 24·5 | 23·75 | 22·3 |
| CaO, HO .... | 37 | 100·00 | 100 | 100·0 „ 100·0 | 100·00 | 100·0 |

*β.* LIME-WATER.—Slaked lime is stirred up in water, and the liquid filtered out of contact of air. As native carbonate of lime, from whatever formation it may be obtained, contains potash and soda salts, the water with which the slaked lime is first treated always takes up potash and soda in the caustic state and in the form of sulphates and chlorides. The water is thereby rendered more alkaline to the taste, and more powerful in its action on vegetable colours; and the formation of carbonate of lime on its surface by exposure to the air likewise takes place more slowly than with pure lime-water. In order therefore to obtain pure lime-water, milk of lime must be first stirred up with water; the solution decanted after subsidence, and the undissolved hydrate of lime mixed with a fresh portion of water, and filtered. (Kuhlmann, *Ann. Pharm.* 38, 48; A. Vogel, *J. pr. Chem.* 25, 230.) According to Dalton (*System*, 2, 331), lime dissolves in 778 parts of water at 15·6°; in 972 parts at 54·4°; and in 1270 parts at 100°; according to Phillips (*Ann. Phil.* 17, 107), in 656 parts of water at 0°; in 752 parts at 15·6°; and in 1280 parts at 100°; hence lime-water saturated at 0° deposits at 100° a considerable quantity of hydrate of lime in small crystals. (Phillips.) 2000 parts of lime-water saturated in the cold, mixed with 1000 parts of water, deposit at 100° one part of hydrate of lime; but with 2000 parts of water, only 0·075 parts, in the form of a slight cloud. When the boiled lime-water is allowed to cool, the precipitate formed by boiling is not redissolved to any perceptible extent. (Graham, *Phil. Mag. Ann.* 2, 23.) ¶ According to Wittstein (*Repert. Pharm.* I., 182), one part by weight of lime dissolves in 729—733 parts of water at ordinary temperatures, and in 1310—1350 parts of boiling water: he also finds that the deposit which settles down when lime-water is exposed to the air consists of $CO_a$, $CO^2$. ¶

Lime-water is colourless, with a slightly alkaline and acrid taste, and becomes covered in the air with a film of carbonate of lime.

*Milk of Lime and Cream of Lime* are mixtures of hydrate of lime and lime-water of different degrees of thickness.

*b.* With acids lime forms the LIME-SALTS. The insoluble salts of this class were formerly called *Selenites*. Lime-salts are colourless if the acid itself is colourless; they have a lower specific gravity than the salts of baryta and strontia, and an acrid taste. A few only of the lime-salts—the hydro-

chlorate more especially—when heated in the blowpipe flame on platinum wire, impart a red colour to the flame, similar to that produced by hydrochlorate of strontia, but less intense. The colour disappears as soon as the salt becomes dehydrated; when chloride of barium is mixed with the chloride of calcium, the red colour is not produced at all. Alcohol burned on soluble lime-salts exhibits a red flame, as with salts of strontia, but tinged with yellow. Lime produces salts nearly or quite insoluble in water, with almost the same acids as baryta and strontia. These salts, however, dissolve readily in hydrochloric and nitric acids, except the sulphate of lime, which is but slightly soluble in these acids. The aqueous solution of a lime-salt gives a precipitate of hydrate of lime with caustic potash or soda, but not with ammonia. White precipitates, easily soluble in hydrochloric acid, are also produced with monocarbonate, biborate, diphosphate, diarsenite, or diarseniate, neutral tartrate, or citrate of soda. Bicarbonate of potash gives no precipitate with dilute solutions, except with the aid of heat. Sulphuric acid does not precipitate a moderately dilute solution, or produces needles only after a considerable time, especially on the addition of alcohol; but in more concentrated solutions, it forms a much more voluminous precipitate than with baryta or strontia-salts. When a salt of lime is precipitated by a quantity of sulphuric acid not sufficient for complete saturation, the filtrate renders a solution of a baryta or strontia-salt turbid, because it contains sulphate of lime in solution. If the precipitated sulphate of lime be well washed and boiled with a large quantity of water, the filtrate likewise gives a cloud with salts of baryta or strontia, and also with oxalate of ammonia or potash. Water saturated in the cold with sulphate of potash gives no immediate precipitate, even in the concentrated solution of a lime-salt. Tungstate of soda separates lime from its salts completely, even when the acid is somewhat in excess. (Anthon.) Oxalic acid, and more especially its soluble salts throw down from salts of lime—even when largely diluted—a white powder, somewhat soluble in hydrochloric and nitric acids, but almost insoluble in acetic acid. Nitrate of lime, dissolved in the proportion of one part of lime to 25,000 parts of water, gives with neutral oxalate of ammonia and with diphosphate of soda, a moderate precipitate; with carbonate of soda, a slight cloud, appearing only after the lapse of five minutes. With 50,000 parts of water, the precipitate produced by the first two salts is scanty, and the cloud with carbonate of soda very slight, appearing only after a considerable time. With 100,000 parts of water an opalescence is produced by the first two salts after five minutes; by carbonate of soda, after a long while, a scarcely perceptible opalescence. With 200,000, 400,000, and 800,000 parts of water, phosphate and carbonate of soda cease to produce any effect; oxalate of ammonia, on the contrary, after 5, and 8, or 15 minutes, produces a slight opalescence, scarcely perceptible with the last-mentioned degree of dilution. (Lassaigne, *J. Chim. Med.* 8, 525.) Oxalate of ammonia produces an immediate cloud in a solution of chloride of calcium containing one part of lime in 400,000 parts of water. (Harting, *J. pr. Chem.* 22, 50.) Only the most concentrated lime solutions yield a white flocculent precipitate with ferrocyanide of potassium; and a crystalline precipitate with iodate or succinate of soda, the latter appearing after some time. The following reagents give no precipitate, even in the most concentrated lime solutions: perchloric acid, hydrofluosilicic acid, sulphide of hydrogen and ammonium, neutral chromate and bichromate of potash, and ferridcyanide of potassium.—Lime also *forms* double salts.

*c.* With some of the earths, forming minerals, glass-fluxes, and enamels.

*d.* With some oxides of the heavy metals, as with oxide of lead.

*e.* With certain organic substances.

### B. Peroxide of Calcium.

Prepared only in the form of *hydrate*, which falls down in very fine scales, when lime-water is mixed with aqueous solution of peroxide of hydrogen, or in excess with nitrate or hydrochlorate of peroxide of hydrogen. (Thénard, *Ann. Chim. Phys.* 8, 313.)

### Calcium and Carbon.

A. Carbonate of Lime.—*a. Dicarbonate.*—Neutral carbonate of lime exposed to a moderate red heat loses only about half its acid. Thoroughly burnt lime placed between slightly ignited charcoal, reabsorbs half the carbonic acid which it has lost. This compound loses all its carbonic acid when strongly ignited (contrary to the statement of lime-burners, who maintain that half-burnt lime cannot be perfectly burnt by subsequent ignition). It effervesces and evolves considerable heat with acids. (Fuchs.) Burnt lime, heated to whiteness in a porcelain tube through which carbonic acid is passed, absorbs carbonic acid at the very temperature at which carbonate of lime, if ignited alone, would give up its acid; it becomes more solid, no longer slakes when moistened with water, and effervesces strongly with acids. (Petzholdt.) It has not yet been determined whether dicarbonate or simple carbonate of lime is produced by this process.

*Hydrated Dicarbonate.*—1. Half-burnt lime does not slake with water, but is hardened by it.—2. *Disintegrated Lime.* Well-burnt lime, exposed to the air, increases sensibly in weight during the first few days; after three months it ceases to do so, and is then changed into the compound mentioned under 2.—This compound gives out much heat while dissolving in hydrochloric acid. After strong ignition it leaves burnt lime, which crumbles to powder when put into water; but the action takes place slowly and without sensible rise of temperature. It is therefore a kind of dead-burnt lime. (Fuchs, *Pogg.* 27, 601.)

| | Anhydrous. | | | Hydrated. | | Fuchs, 2. |
|---|---|---|---|---|---|---|
| 2CaO | 56 | 71·79 | 2CaO | 56 | 64·37 | 63·8 |
| $CO^2$ | 22 | 28·21 | $CO^2$ | 22 | 25·29 | 24·0 |
| | | | HO | 9 | 10·34 | 12·2 |
| $2CaO, CO^2$ | 78 | 100·00 | $CaO, HO + CaO, CO^2$ | 87 | 100·00 | 100·0 |

*b. Monocarbonate.*—Found abundantly in nature in the form of calc-spar, marble, limestone, stalactitic limestone, and chalk; also in oyster shells, egg shells, bones, &c. Anhydrous lime does not absorb carbonic acid, even after exposure to the air for a week, provided no water has access to it. (Scheele.) Lime-water and hydrate of lime attract it with great avidity. This salt is obtained in the purest state possible, by dissolving ignited oyster shells in hydrochloric acid, precipitating the phosphate of lime by ammonia, filtering, precipitating with carbonate of ammonia, and washing thoroughly. It can be obtained in the crystalline form, by a method similar to that employed for carbonate of baryta. (III. 139) (Zoega.)

Carbonate of lime is dimorphous, and crystallizes in the forms of Calcspar and Arragonite. The crystalline system to which *Calcspar* belongs is the rhombohedral, *Fig.* 141 (the primitive form is the obtuse rhombohedron), 137, 138, 139, 140, 142, 143, 146, 147, 148, 149, 150, 151, 152, 154, and some hundred other forms, among which are many acute and obtuse rhombohedrons; $r^3 : r^5$ in Fig. 141 = 104° 28′ 40″; $r^1 : r^3$ or $r^5 = 75° 31′ 20″$; $p : r$ (*Figs.* 137 and 139) = 135°; $r : s = 127° 45′ 40″$; $r : \sigma = 135°$; $s : s$ or $\sigma : \sigma = 120°$: $\mu : \mu^1$ (*Fig.* 147 and 148) = 144° 20′ 26″, and so on. (Hauy.) Easily cleft in the direction of the *r*-surfaces. (*Fig.* 141.) Specific gravity of Iceland-spar (double refracting spar) = 2·717 in vacuo (Le Royer & Dumas), = 2·721 (Mohs), = 2·75 (Neumann); of the most acute rhombohedron of calcspar = 2·6987; of the moderately acute rhombohedron (*Fig.* 141) = 2.700; of the most obtuse = 2·7064. (Karsten.)

The crystals of *Arragonite* belong to the right prismatic system. *Fig.* 54 (primary form), 55, and other forms; $i : u = 107° 49′$; $u : u^1 = 64° 4′$; $u : t = 122° 2′$. (Hauy.) Sp. gr. = 2·931 (Mohs), = 2·995. (Breithaupt.) When gently heated, it becomes opaque without loss of weight; throws out cauliflower-like excrescences, and crumbles to powder: because the atoms take up a new arrangement and unite in the form in which they exist in calcspar. (Berzelius, Mitscherlich, *Pogg.* 21, 157.)

The artificially prepared salt generally has the form of a white powder, consisting of small crystals, which take the form and specific gravity of calcspar or arragonite, according to the circumstances under which they are produced. (I., 100, 101.) Both natural and artificial carbonate of lime may be fused to a fine-grained mass, consisting of crystals of calcspar and resembling marble, by being strongly pressed into a crucible, and exposed to a strong heat; the loss of carbonic acid often amounts to only one per cent. (Hall, Bucholz, *N. Gehl.* 1, 271.) Carbonate of lime is tasteless, and has a slight alkaline reaction on vegetable colours. Marble, chalk, or arragonite, in fine powder, turns reddened litmus blue, and violet juice green. (Laugier, *J. Chim. Med.* 6, 225; Pleischl, *Zeitschr. Phys.* v. W. 5, 54.)

| | Calculation. | | Berthollet. M. & K. | Kirwan. | Schaffgotsch. K. | Schaffgotsch. D. | Erdmann & March. K. | Dumas. D. | Marcet. |
|---|---|---|---|---|---|---|---|---|---|
| CaO ..... | 28 | 56 | 53·65 | 55 | 55·88 | 55·84 | 56 | 56·06 | 56·1 |
| $CO^2$ ..... | 22 | 44 | 46·35 | 45 | 44·12 | 44·16 | 44 | 43·94 | 43·9 |
| CaO, $CO^2$ | 50 | 100 | 100·00 | 100 | 100·00 | 100·00 | 100 | 100·00 | 100·0 |

| | Stromeyer. D. | Berzelius, Ure. | Thénard. D. | Thomson. | Bucholz. D. | Richter. | Bergman. |
|---|---|---|---|---|---|---|---|
| CaO..... | 56·23 | 56·4 | 56·68 | 56·86 | 56·5 | 55·9 | 55 |
| $CO^2$..... | 43·77 | 43·6 | 43·32 | 43·14 | 43·0 | 44·1 | 34 |
| Water .... | | | | | 0·5 | | 11 |
| | 100·00 | 100·0 | 100·00 | 100·00 | 100·0 | 100·0 | 100 |

D signifies Iceland spar; M, Carrara marble; K, artificial carbonate of lime. Arragonite generally contains from $\frac{1}{2}$ to 4 per cent. of carbonate of strontia (Stromeyer, *Untersuch. der Mineralkörper*, 98), and more rarely 2 to 4 per cent. of carbonate of lead. (Böttger, Karsten, *Pogg.* 47, 497; 48, 352.)

Carbonate of lime is decomposed at a full red heat into lime and carbonic acid; if vapour of water, or any other kind of vapour or gas has access to it, a lower temperature will suffice. If it be heated in a

tube till it begins to evolve carbonic acid, the heat then lowered till the evolution almost ceases, and vapour of water passed through the tube, the evolution of carbonic acid immediately recommences, but is arrested as often as the current of vapour is cut off. The aqueous vapour drives out the atmosphere of carbonic acid gas which surrounds the carbonate of lime; and, by its pressure, hinders the evolution of carbonic acid [or, according to the other view (I., 21, 22, and 125, 126), the adhesion of the aqueous vapour to the carbonic acid gas favours its evolution]. A current of air acts in the same manner as steam. Moistening the limestone with water, however, does not accelerate its burning, but rather retards it and wastes the fuel, because most of the water evaporates before the evolution of carbonic acid commences. (Gay-Lussac, *Ann. Chim. Phys.* 63, 219; also *Ann. Pharm.* 22, 52; also *J. pr. Chem.* 11, 244.) A mixture of equal parts of carbonate of lime and powdered quartz, exposed to a white heat for three-quarters of an hour in a loosely covered crucible, yields, after being moistened, a highly alkaline mass, from which hydrochloric acid dissolves, together with the lime, a large quantity of silica which had combined with the lime. But when the same mixture is put into a strong wrought-iron bottle—the bottle being completely filled with it, and closely screwed down—and exposed for an hour and a half to the heat of a blacksmith's forge,—a greyish white powder is obtained, which, when moistened, scarcely reddens turmeric, and dissolves in hydrochloric acid, with rapid evolution of carbonic acid, leaving nearly all the quartz behind. (Petzholdt, *J. pr. Chem.* 17, 464; *compare* Vol. I., 128.) 2 parts of powdered carbonate of lime disposed in alternate layers in a glass tube with one part of sodium, and heated, yields with vivid inflammation, a black mass, which leaves a residue of carbon when treated with hydrochloric acid. (Gay-Lussac & Thénard, *Recherch.* 1, 364; Döbereiner, *N. Br. Arch.* 18, 155.) A concentrated solution of potash withdraws carbonic acid from lime. (Liebig, *Pogg.* 24, 366.) Carbonate of lime dissolves in aqueous solutions of ammoniacal salts, and less readily in salts of potash. Carbonate of lime just precipitated (amorphous), dissolves easily in a cold concentrated solution of sal-ammoniac; but after being precipitated 24 hours, it dissolves with difficulty; pulverized calcspar or marble is still less soluble. These solutions become turbid in the air, but do not deposit the whole of the lime which they contain. (A. Vogel, *J. pr. Chem.* 7, 453.) Recently precipitated carbonate of lime is readily soluble in an aqueous solution of carbonate, sulphate, hydrochlorate, nitrate, or succinate of ammonia; the solution in the first-mentioned salt becomes turbid immediately (one part of lime-salt requiring for permanent solution, 65,246 parts of carbonate of ammonia); the solution in the others remains clear. When the precipitated carbonate of lime has assumed a crystalline form from long standing, it gives only turbid solutions with the above-mentioned salts, even with the aid of heat. (Wittstein, *Repert.* 57, 18.) One atom of carbonate of lime boiled in water for a considerable time with one atom of sal-ammoniac—the water which evaporates being constantly renewed—is almost entirely dissolved, with evolution of carbonate of ammonia, the solution ultimately retaining but a small quantity of ammonia. (D. Smith.) Lime-water rendered turbid by carbonic acid, again becomes clear on the addition of sulphate of potash or chloride of potassium. (G. Morveau.) In pure water, carbonate of lime is but very slightly soluble; but dissolves more readily in cold water than in hot. ¶ Fresenius states (*Ann. Pharm.* 59, 117), that one part of carbonate of lime is soluble in 8834 parts of boiling water, and

only in 10,601 parts of water at ordinary temperatures. ¶ The solution has a slight alkaline reaction. Water boiled with pounded marble or chalk turns reddened litmus blue. (Laugier, Pleischl.) If lime-water is precipitated with a quantity of carbonic acid less than sufficient for saturation, the filtrate, when boiled out of contact of air, deposits an additional quantity of carbonate of lime. (A. Vogel, *Schw.* 33, 207.)

*Hydrated Carbonate of Lime.*—¶ Found native by Scheerer (*Pogg.* 58, 382), in a running stream, in the form of small rhombohedral crystals, which, after drying between folds of bibulous paper, contained 48 per cent. of water, the remaining portion consisting of carbonate of lime with small quantities of magnesia, silica, alumina, iron, and organic matter. The formula for this compound would be $CaO, CO^2 + 5Aq$. ¶ 1. The liquid obtained by boiling about one part of lime and 3 parts of sugar in 6 parts of water—after exposure to the air for some months in a cold place—deposits crystals which may be washed with cold water. Similar results are obtained with solutions of lime in sugar of milk, gum, or starch water. (Pelouze, *Ann. Chim. Phys.* 48, 301; also *Pogg.* 24, 575; also *Ann. Pharm.* 2, 228.) 2. A solution of lime in sugar and water, exposed to the influence of a galvanic battery of 12 pair of plates, deposits the same crystals on the positive platinum electrode. (Becquerel.) 3. In the copper tube of a pump, crystals of the same kind were deposited from the spring water. (Prince of Salm-Horstmar.)

Very acute rhombohedrons, of specific gravity 1·783; tasteless (Pelouze); rhombic prisms with dihedral summits, as in arragonite, *Fig.* 54; $u : u = 83$ to 84° nearly (Becquerel); irregular six-sided prisms of specific gravity 1·75. (Salm-Horstmar.)

The salt dried in the air is reduced to a pasty consistence by rubbing in a mortar, but again becomes dry if the operation be long continued; it becomes opaque in the air at a temperature above 19°, and crumbles to a white powder; under water it remains unchanged below 17·5°; but close upon 19°, it crumbles to the same white powder. (Salm-Horstmar.) It loses its water between 20° and 30°, and becomes doughy; but below 20° it remains unaltered in the air. In water or ether at 30° it crumbles to a fine, chalky powder. Boiling hydrated alcohol withdraws the water from it entirely; but boiling absolute alcohol deprives it of only 2 atoms of water: the crystals do not lose their form in this process, but become disintegrated; and if dried at 5° still retain 34·8 per cent. (3 At.) of water; when exposed to the air, they rapidly effloresce. (Pelouze.)

| | Calculation. | | | Pelouze. | Salm-Horstmar. |
|---|---|---|---|---|---|
| CaO | 28 | 29·47 | .... | 52·92 | .... 29·54 |
| $CO^2$ | 22 | 23·16 | | | 18·40 |
| 5HO | 45 | .... 47·37 | .... | 47·08 | .... 47·38 |
| Impurities | | | | | 3·30 |
| $CaO, CO^2 + 5Aq.$ | 95 | .... 100·00 | .... | 100·00 | .... 98·60 |

*c. Acid Salt.*—Carbonate of lime dissolves in aqueous solution of carbonic acid. Saturated lime-water is rendered turbid by carbonic acid gas; but on passing more of the gas through it, the opacity nearly disappears; more water, however, must be added in order to obtain a perfectly clear solution. Bicarbonate of ammonia, potash, or soda precipitates lime-salts; but less completely in proportion as the quantity of water present is greater. (Val. Rose, *N. Gehl.* 3. 548.) This compound reddens

litmus, but turns logwood and mallows blue, and turmeric or rhubarb, brown, even when the carbonic acid is in large excess (Morveau, Dalton, Pfaff, *Schw.* 34, 122). It turns reddened litmus blue. (Pleischl, *Zeitschr. Phys. v. W.* 5, 57.) When free from excess of carbonic acid, it turns litmus and mallows blue, but does not redden turmeric; with excess of carbonic acid it turns mallows blue, but litmus red. (Gm.) It evolves carbonic acid by exposure to the air or when heated to the boiling point, monocarbonate of lime being precipitated; *Boiler incrustations* (*Kesselstein*).

## Calcium and Boron.

Borate of Lime.—Borax gives with lime-water a white, tasteless precipitate difficultly suluble in water. (Bergman, *Opusc.* 3, 363.) Borax precipitates solutions of lime-salts when not too dilute. When a solution of borax is added to a warm solution of chloride of calcium, the precipitate first formed always re-dissolves; with a large quantity of borax solution it remains permanent, and unites together in a soft mass. (Berzelius.) The precipitate fuses in the fire to a glass. It is scarcely soluble in pure water, but readily dissolves in water containing sal-ammoniac or chloride of calcium. Sex-borate of potash also precipitates lime-salts. (Laurent.) Probably the borate, biborate, and sexborate of lime have yet to be distinguished. The precipitate which nitrate of lime gives with borax is biborate of lime, and has, according to Tünnermann (*Kastn. Arch.* 20, 50), the following composition:

| | Ignited. | | Tünnermann. |
|---|---|---|---|
| CaO ..... | 28·0 .... | 28·69 ..... | 30·17 |
| $2BO^3$ ..... | 69·6 .... | 71·31 ..... | 69·83 |
| * $CaO,2BO^3$ | 97·6 .... | 100·00 ..... | 100·00 |

| | Dried in the air. | | Tünnermann. |
|---|---|---|---|
| CaO ..... | 28·0 .... | 26·27 ..... | 26·4 |
| $2BO^3$ ..... | 69·6 .... | 65·29 ..... | 61·1 |
| HO ..... | 9·0 .... | 8·44 ..... | 12·5 |
| + HO ..... | 106·6 .... | 100·00 ..... | 100·0 |

*Rhodizite* also appears to consist of borate of lime. (*Vid.* G. Rose, *Pogg.* 33, 253; and 39, 321.)

## Calcium and Phosphorus.

A. Phosphide of Calcium.—Formerly called *Phosphuret of Lime.*—Obtained mixed with phosphate of lime, by bringing together phosphorus and lime at a low red heat. According to Dumas (*Ann. Chim. Phys.* 33, 363), 28 parts (1 atom) of red-hot lime take up at most 16 parts ($\frac{1}{2}$ atom) of phosphorus. Since, however, according to H. Rose, an admixture of uncombined lime is scarcely to be avoided—because the compound again loses part of its phosphorus when too strongly heated—we may perhaps assume that 8 atoms of lime require 6 atoms of phosphorus for complete saturation. The following formula would coincide with this supposition:

$$8CaO + 6P = 3CaO,cPO^5 + 5CaP.$$

One part of dry phosphorus is placed at the closed end of a glass tube,

and 5 parts of well-burnt lime in small pieces in the middle: this portion of the tube is gently ignited, and when the lime is at a low red heat, the phosphorus is made to boil. The vapour of the phosphorus is absorbed by the lime with vivid incandescence. (Pearson.) Von Mons projects phosphorus into a heated glass flask containing powdered lime. The variety which contains the larger quantity of phosphorus is black, but has no metallic lustre; that which contains the smaller quantity is reddish-brown. The black variety, when gently ignited out of contact of air, loses part of its phosphorus, and is converted into the brown: in an atmosphere of hydrogen, the change takes place at a much lower temperature. Both varieties lose all their phosphorus at a strong red heat, and leave pure lime. (H. Rose, *Pogg.* 12, 543.) This is an instance of reciprocal affinity arising from the increasing affinity of heat for phosphorus at a higher temperature. The mixture burns when heated in the air and forms phosphate of lime. It causes hypochlorous acid gas to explode at ordinary temperatures, and is converted by aqueous hypochlorous acid into phosphate of lime, with evolution of chlorine. (Balard.) In a current of chlorine gas it yields pentachloride of phosphorus, chloride of calcium, phosphate of lime and free lime (previously contained in the mixture). (Dumas, H. Rose.) Heated in a flask with excess of sulphur, till all the sulphur which does not enter into combination is volatilized, it leaves sulphide of calcium, phosphate of lime, and sulphate of lime (this last is produced by the action of the free lime on the sulphide of calcium; *H. Rose.*) With water it is decomposed with violent effervescence into spontaneously inflammable phosphuretted hydrogen gas, and hypophosphite and phosphate of lime. The monophosphide of calcium assumed to be present in the compound, together with phosphate of lime, is evidently decomposed thus:—

$$2CaP + 3HO = 2CaO,PO + PH^3.$$

The mixture decomposes slowly in the air in precisely the same manner, emitting phosphuretted hydrogen gas. With concentrated hydrochloric acid it deposits phosphorus, and evolves difficultly inflammable phosphuretted hydrogen gas, sometimes pure, sometimes contaminated with from one to five per cent. of hydrogen gas; with dilute hydrochloric acid it yields pure phosphuretted hydrogen gas, but more slowly and with less heat. (Dumas.) Possibly in this manner:

$$3CaP + 3HCl = 3CaCl + PH^3 + 2P.$$

Powdered lime stirred up with phosphorus in a glass flask at a temperature of about 150°, yields a yellow powder which inflames spontaneously in the air, thus answering the purpose of a match. Probably a mere mixture of lime and phosphorus.

B. Hypophosphite of Lime.—1. Phosphorus is thrown gradually in small pieces into boiling milk of lime, the water which evaporates being replaced and the ebullition kept under till the phosphorus has disappeared, and the strong smell of phosphuretted hydrogen gas has passed off; the filtrate is then freed from excess of lime by passing carbonic acid through it; the acid carbonate of lime formed is decomposed by a gentle heat; and the filtered solution evaporated either in vacuo over oil of vitriol, or in the air with the aid of heat. The latter method yields finer crystals; but these, on dissolving in water, deposit a white powder *consisting partly of* phosphate of lime. (H. Rose, *Pogg.* 9, 364; 12. 79.)

The milk of lime is very apt to boil over with the phosphorus; it must, however, be kept constantly at the boiling point; because if it be allowed to cool, air will enter the vessel and explode with the phosphuretted hydrogen. The crystals are obtained by evaporation. (Wurtz, *Ann. Pharm.* 43, 322.)—2. Phosphide of calcium is decomposed by boiling water—digested for some time—and the filtrate treated with carbonic acid, &c., as in the first method; the crystals are obtained by slow evaporation. (Bachmann, *Zeitschr. Phys. Math.* 3, 24.)

Colourless rectangular prisms with terminal faces obliquely inclined to the two broad lateral faces; easily cleft in the direction of the broad lateral faces. These faces have a strong pearly lustre, whereas the others which are less smooth are of a glassy lustre. It is more flexible than gypsum. (H. Rose.) It belongs to the oblique prismatic system, forming oblique irregular six-sided prisms (*Fig.* 103, without the *m*-face) which are permanent in the air. (Wurtz.) Has a nauseous bitter taste. (Bachmann.)

| | Crystallized. | | | Wurtz. | Bachmann. | H. Rose. |
|---|---|---|---|---|---|---|
| CaO | 28·0 | .... | 32·79 | 33·06 | .... 31·7 | |
| PO | 39·4 | .... | 46·13 | 45·94 | | |
| 2HO | 18·0 | .... | 21·08 | 21·00 | .... 20·1 | .... 18·76 to 22·18 |
| CaO,2HO,PO | 85·4 | .... | 100·00 | 100·00 | | |

The crystals analyzed by Bachmann were dried at a temperature above 100°; he found them, at the same time, to contain 34·8 per cent. of phosphorus and 13·4 per cent. of oxygen. The crystals obtained in vacuo yielded in H. Rose's experiments 22·18 per cent. of water; those obtained by ordinary evaporation, little more than 18 per cent. Rose regards part of this water as mechanically combined, and supposes the crystals to contain only 1½ atom of chemically combined water.

The crystals do not lose any water at 300°. (Wurtz.) Heated to redness in a retort, they decrepitate, evolve water, and afterwards give off spontaneously inflammable phosphuretted hydrogen gas, which, towards the end of the process becomes difficultly inflammable from being partially decomposed by a portion of phosphorus which sublimes. A reddish kind of residue is left, amounting to 79·97 per cent., and containing 2 atoms of lime with rather more than 1 atom of phosphoric acid, together with a small quantity of oxide of phosphorus. (H. Rose.)

$$2(CaO,PO,2HO) = 2CaO,PO^5 + PH^3 + HO.$$

That rather more than half of the phosphorus should remain behind with the lime in the form of phosphoric acid is accounted for by H. Rose, on the supposition that the air in the retort causes the formation of a portion of phosphoric acid. More than 1 atom of water appears also to be decomposed; for, according to Wurtz, but little water passes over; and the phosphuretted hydrogen gas evolved is mixed with about an equal volume of hydrogen, which at last comes over nearly pure. The crystals oxidized by means of nitric acid leave, after ignition, 114·68 per cent. of metaphosphate of lime. (H. Rose.) The salt inflames when a small quantity of fuming nitric acid is poured on it; detonates with a mixture of chlorate of potash and powdered quartz, and instantly reduces nitrate of silver. (Bachmann.) It is soluble in 6 parts of cold, and not much less of hot water. (Wurtz, H. Rose.) It is not dissolved by strong alcohol, and very sparingly when the alcohol is dilute. (H. Rose.)

C. Diphosphite of Lime.—Separates on mixing an aqueous solution of *phosphite of ammonia* with chloride of calcium, as a white

crystalline crust, but not till after some time. (H. Rose.) Crystallizes from an aqueous solution by slow evaporation. (Dulong.) When ignited, it evolves pure hydrogen gas, with a trace of water, and leaves diphosphate of lime of a brownish colour. (H. Rose, *Pogg.* 9, 26.) An aqueous solution is decomposed by boiling into a precipitated basic salt [triphosphite?] of a pearly lustre, and a difficultly crystallizable acid salt [monophosphite?] which remains dissolved. (Dulong.)

Calculation, according to H. Rose.

| | | |
|---|---|---|
| 2CaO | 56·0 | 43·28 |
| $PO^5$ | 55·4 | 42·81 |
| 2HO | 18·0 | 13·91 |
| 2CaO, $PO^5$, 2HO | 129·4 | 100·00 |

D. Ordinary Phosphate of Lime.—*a. Tri-phosphate.—Bone Earth, Animal Earth.*—Found in combination with chloride or fluoride of calcium in apatite, and mixed with carbonate of lime, &c. in the ashes of bones and many other animal and vegetable substances.—*Preparation.*—1. Chloride of calcium mixed in solution with ammonia is precipitated by diphosphate of ammonia. (Fuchs.)—2. Chloride of calcium is precipitated by excess of diphosphate of ammonia or soda. In this case, the supernatant liquid becomes acid from the formation of monophosphate of ammonia or soda.

$$3(CaO, HCl) + 2(2NH^3, PO^5) = 3CaO, PO^5 + 3(NH^3, HCl) + NH^3, PO^5.$$

(Mitscherlich.)—3. Bone-ash is dissolved in hydrochloric or nitric acid, the carbonic acid expelled by boiling, and then the solution precipitated by ammonia. The precipitate forms in very voluminous and gelatinous flakes, and when dried after washing, cakes together in a white amorphous mass, of conchoidal fracture. According to Saussure, it fuses at 378° Wedgw. to a substance resembling porcelain.

| | Calculation. | | Berzelius. | | Fuchs. | | Thilenius. | |
|---|---|---|---|---|---|---|---|---|
| 3CaO | 84·0 | 54·05 | 51·68 | | 54·35 | | 57·44 | |
| $cPO^5$ | 71·4 | 45·95 | 48·32 | | 45·65 | | 42·56 | |
| 3CaO, $cPO^5$ | 155·4 | 100·00 | 100·00 | | 100·00 | | 100·00 | |

Berzelius regards this salt as $8CaO, 3PO^5$, and states that the triphosphate can only be obtained by digesting it with caustic soda (and not with ammonia) or by precipitating chloride of calcium with triphosphate of soda. ¶ In a more recent examination, Berzelius (*Ann. Pharm.* 53, 286) has arrived at the following results: 1. When a solution of phosphate of ammonia supersaturated with ammonia, is treated with a solution of chloride of calcium till about half the phosphoric acid is precipitated, the precipitate formed contains 51·263 per cent. of lime, which corresponds to the formula $8CaO, 3PO^5$.—2. On adding an excess of chloride of calcium to the filtrate, and leaving the precipitate obtained in contact with the solution for 24 hours before filtering, the compound is found to contain 53·34 per cent. of lime, which nearly corresponds with the formula $3CaO, PO^5$.—3. When a solution of chloride of calcium is mixed with excess of ammonia, and a quantity of phosphate of ammonia added insufficient to precipitate the whole of the lime, the precipitate consists of $3CaO, PO^5$. This precipitate is less gelatinous, and nearly twice as opaque as the preceding; when dried and ignited it has an earthy fracture, that of the former being harder and somewhat brilliant. Hence Berzelius concludes that the composition of the phosphate of lime in bones must be a subject of uncertainty,

inasmuch as both the preceding phosphates of lime would be precipitated, and in variable proportions, on adding ammonia in excess to a solution of the bone-earth in hydrochloric acid. ¶ Fuchs (*Schw.* 24, 124) by dissolving 100 parts of Iceland spar in hydrochloric acid, and precipitating with phosphate of ammonia and excess of ammonia, obtained after ignition 103·04 parts of phosphate of lime; this salt, therefore—assuming 56 per cent. of lime in the calc-spar—contained 54·35 per cent. of lime (56·4 would give 54·74 per cent.; see also Mitscherlich, *Lehrb.* 2, 135.)

The salt gently heated with potassium yields a phosphide of the metal, which evolves phosphuretted hydrogen gas when moistened with acidulated water. (Vauquelin & Thénard, *J. Chim. Med.* 1, 17.)—A mixture of phosphate of lime with silica and charcoal is resolved at a white heat into silicate of lime, phosphorus, and carbonic oxide. 10 parts of phosphate of lime heated to whiteness with 5 parts of quartz and 5 parts of clay in a charcoal crucible, evolve 3 parts of phosphorus, amounting to about $\frac{3}{5}$ of the whole; the quantity evolved increases in proportion to the amount of silica employed. (Berthier, *Ann. Chim. Phys.* 33, 179.) Upon this is founded Wöhler's method of preparing phosphorus (II., 104). The same fact explains the observation of Saussure, *viz.*, that phosphate of lime mixed with charcoal, at a white heat, evolves phosphorus; the silica contained in the charcoal and the retort doubtless aiding in its disengagement.

When digested with dilute sulphuric acid, the salt swells up and is resolved into sulphate of lime, and a soluble compound of phosphoric acid with a small quantity of lime, or free phosphoric acid, according to the proportion of sulphuric acid employed.—155·4 parts (one At.) of triphosphate of lime with 98 parts (2 At.) of oil of vitriol, yield sulphate and monophosphate of lime—

$$3CaO, PO^5 + 2SO^3 = 2(CaO, SO^3) + CaO, PO^5;$$

with 147 parts (3 At.) of oil of vitriol, sulphate of lime and free phosphoric acid are the result.

$$3CaO, PO^5 + 3SO^3 = 3(CaO, SO^3) + PO^5.$$

A portion of gypsum, however, remains dissolved in the phosphoric acid set free, its quantity increasing with the amount of water present; but it may be precipitated, by a large addition of alcohol (*vid.* II., 129). Döbereiner and Berzelius have shown that the lime may be totally separated from the phosphoric acid by the addition of a sufficient quantity of sulphuric acid. Hydrochloric and nitric acids readily dissolve triphosphate of lime, converting it at the same time into the monophosphate by withdrawing 2 atoms of lime. Crum (*Ann. Pharm.* 63, 394) has extended this observation likewise to many of the vegetable acids, as the tartaric, acetic, malic, and lactic acids, with the same results. From this solution, acetate of lead precipitates the phosphoric acid as phosphate of lead (accompanied by chloride of lead when hydrochloric acid is employed). Glacial acetic acid precipitates monophosphate of lime from a solution of the salt in nitric acid, nitrate of lime remaining in solution. (Persoz, *Chim. Molecul.* 346.)

*Solvent powers of hydrochloric and nitric acids of different degrees of dilution, at 17° according to G. Bischof* (*Schw.* 67, 39).—*a.* One part of hydrochloric acid of specific gravity 1·153 is mixed with the quantities of water specified; similarly, one part of nitric acid of specific gravity 1·23. —*b.* One part of lime-salt, if added in excess, is dissolved by the stated quantity of the *mixture*.—*c.* *100* parts of hydrochloric acid of specific

gravity 1·153, and 100 parts of nitric acid of specific gravity 1·23, dissolve the following quantities of the lime-salt according to their degree of dilution.

| Hydrochloric Acid. | | | Nitric Acid. | | |
|---|---|---|---|---|---|
| *a.* Parts of Water. | *b.* Parts of the Mixture. | *c.* Parts of Lime-Salt. | *a.* Parts of Water. | *b.* Parts of the Mixture. | *c.* Parts of the Lime-Salt. |
| 0 | 3·95 | 25·32 | 0·000 | 2·72 | 36·78 |
| 1 | 4·44 | 45·01 | 0·827 | 4·23 | 43·23 |
| 4 | 8·12 | 62·31 | 3·309 | 10·25 | 42·05 |
| 7 | 12·35 | 64·75 | 5·791 | 15·45 | 43·95 |
| 10 | 15·97 | 68·90 | 8·273 | 20·34 | 45·59 |
| 13 | 19·47 | 71·91 | 10·000 | 20·82 | 52·83 |
| 16 | 24·44 | 69·55 | 10·756 | 30·64 | 56·94 |
| 19 | 28·68 | 69·72 | 13·000 | 26·48 | 52·86 |
| | | | 13·236 | 32·14 | 44·30 |
| | | | 15·718 | 36·06 | 46·37 |
| | | | 40·000 | 127·81 | 37·08 |

[72·8 parts (2 At.) of anhydrous hydrochloric acid should decompose and dissolve 155·4 parts (one At.) of the lime-salt.

$$3CaO, PO^5 + 2HCl = CaO, PO^5 + 2(CaO, HCl);$$

100 parts of aqueous hydrochloric acid of specific gravity 1·153 contain 30·9 parts of anhydrous acid; 72·8 : 155·4 = 30·9 : 66; 100 parts of the aqueous acid of specific gravity 1·153 should therefore, when diluted to any extent, dissolve 66 parts of the lime-salt. With this, the division *c* accords upon the whole; but why the acid when moderately diluted should dissolve more, and when not diluted so much less than 66 parts, remains to be explained. Similar results are obtained with nitric acid: 108 parts (2 At.) of anhydrous acid should decompose 155·4 parts of the salt; 100 parts of acid of specific gravity 1·23 contain 31 parts of the real acid; and 108 : 155·4 = 31 : 44·5.]

Phosphate of lime is slightly soluble in aqueous solutions of ammoniacal salts. The recently precipitated salt is dissolved in small quantity by cold water containing sal-ammoniac (Wöhler, *Pogg.* 4, 166); also by water containing nitrate or succinate of ammonia. (Wittstein.) Even the anhydrous salt is dissolved by long boiling with solution of hydrochlorate, nitrate, or succinate of ammonia (Hünefeld, *Arch. f. d. med. Erfahr.* 1826, 520; Wittstein); in this case ammonia is doubtless evolved.

$$3CaO, PO^5 + 2(NH^3, HCl) = CaO, PO^5 + 2(CaO, HCl) + 2NH^3.$$

Delkeskamp (*Crell. Ann.* 1798, 2, 226) found that phosphate of lime boiled for several hours with sulphate of ammonia, was converted into sulphate of lime, while phosphoric acid passed into the solution; this was also confirmed by Morveau. (*J. Polytechn. Cah.* 3, 434.) [It is not, however, a case of decomposition by double affinity; but sulphate and soluble monophosphate of lime are produced and ammonia evolved].—Phosphate of lime is also sparingly soluble in water holding common salt in solution. (Thomson, *Ann. Phil.* 17, 12.) When recently precipitated, it is also soluble to a very slight extent in pure water, so that the liquid becomes cloudy on the addition of nitrate of lead. (R. Phillips, *Ann. Phil.* 22, 188.) It dissolves more readily in water containing starch or glue. (Vauquelin, *J. Phys.* 85, 126.)

*b. Di-phosphate.*—1. Falls down in very small opaque needles, slightly contaminated, however, with *a*—on dropping a solution of ordinary diphosphate of soda into excess of chloride of calcium. (Berzelius.) If the

diphosphate of soda is in excess, phosphoric acid separates from the precipitate and combines with it, forming monophosphate of soda, and the precipitate is converted into the salt *a*. (Berthollet, *Statique Chim.* 1, 117; Berzelius.)

¶—2. When a solution of chloride of calcium is precipitated with a slight excess of ordinary phosphate of soda—the solution with the precipitate divided into two equal parts—to one portion just enough nitric or hydrochloric acid added, to effect solution without the aid of heat—the other portion then added, and the whole allowed to stand quietly for 48 hours,—the amorphous precipitate of phosphate of lime increases rapidly in density, and is gradually converted into fine white scales, which, under the microscope, present the appearance of thin, tabular, rhombic prisms, with the acute prismatic edges generally replaced by planes, so that the crystals have the appearance of irregular six-sided tables. The compound thus formed is decomposed by boiling in water, and becomes bulky, opaque, and indistinctly crystalline; the supernatant liquid strongly reddens litmus. The formula of the salt is: $2CaO, HO, PO^5 + 4$ Aq. (Bödeker, *Ann. Pharm.* 69, 206.) ¶

Diphosphate of lime when freshly precipitated, expels hydrochloric acid, with the aid of heat, even from a concentrated solution of chloride of calcium, and combines with the lime set free. (Berzelius.) It is not soluble in water, but very easily soluble in aqueous acids, even in aqueous carbonic acid. In this state, it is found in several mineral waters. (Berzelius.)

| | Ignited. | | Berzelius. |
|---|---|---|---|
| $2CaO$ | 56·0 | 43·96 | 45·81 |
| $PO^5$ | 71·4 | 56·04 | 54·19 |
| $2CaO, PO^5$ | 127·4 | 100·00 | 100·00 |

| | Crystallized. | | Berzelius. | Bödeker's salt. |
|---|---|---|---|---|
| $2CaO$ | 56·0 | 34·27 | 35·42 | 32·56 |
| $PO^5$ | 71·4 | 43·70 | 41·90 | 41·22 |
| $4HO$ | 36·0 | 22·03 | 22·68 | 26·22 |
| $2CaO, PO^5, 4HO$ | 163·4 | 100·00 | 100·00 | 100·00 |

c. *Three-fourths Phosphate.*—$4CaO, 3PO^5$.—Aqueous solution of phosphoric acid is saturated with the salt *a*; the solution mixed with alcohol; and the white precipitate formed, washed with alcohol and dried. White powder having an acid taste, and reddening litmus. With water it separates into the insoluble salt *b*, and an acid salt which remains in solution [with one atom of acid ?] (Berzelius, *Ann. Chim. Phys.* 2, 167.) If the salt *a* recently precipitated is immersed in a solution of hydrated phosphoric acid ignited just before it was dissolved in water, it gradually changes to a tenacious acid mass, which may be drawn out into threads, and sticks to the teeth; after drying, it becomes yellow, transparent, and very friable. This substance has the same composition as *c*, and is decomposed in the same manner by water, but contains metaphosphoric acid as well as ordinary phosphoric acid. (Berzelius, *Lehrb.* 4, 277.) Graham regards this compound as metaphosphate of lime.

If one part of fused hydrated metaphosphoric acid is dissolved in 3 parts of water, the solution saturated hot with the salt *a*, and evaporated,—foliated acid crystals are obtained, easily soluble in their own weight of cold water; decomposed by alcohol and by ammonia, which precipitate 50 per cent. of salt *a*; fusing when heated; swelling, up with loss of 22 per cent. of water, and changing into a hard, tasteless mass

insoluble in water or cold nitric acid [metaphosphate of lime]. Consequently, the crystals contain 27 per cent. of lime, 51 of acid, and 22 of water [about $4CaO, 3PO^5 + 9$ Aq.]. (Funcke, *N. Tr.* 8, 2, 17.)

*d. Monophosphate.*—A solution of the salt *a* or *b* in phosphoric, hydrochloric, or nitric acid, is evaporated to the crystallizing point. Small crystalline scales having an acid taste, and becoming moist and viscid in the air. The salt, when ignited, loses water and fuses to a clear glass [of metaphosphate of lime] which is insoluble in water, and when distilled with charcoal gives off a portion of its phosphorus [just two-thirds] in the free state. On this property is founded the ordinary method of preparing phosphorus (II., 104). (Berzelius, *Lehrb.* 4, 276.)

*e. Superphosphate.*—If 155·4 parts of salt *a* or of bone-ash are digested in water and more than 98 but less than 147 parts of oil of vitriol, the liquid, filtered from the gypsum which is produced, contains free phosphoric acid and monophosphate of lime, in variable proportions. If this solution is evaporated and the residue heated to low redness, it leaves a transparent, colourless, hard, readily fusible, and very acid glass. (*Phosphorglas.*) This may perhaps be regarded as a mixture of mono-metaphosphate of lime and hydrate of metaphosphoric acid, the latter of which, when strongly ignited, partly volatilizes.

¶—E. Pyrophosphate of Lime.—Chloride of calcium yields with pyrophosphate of soda a white amorphous precipitate *a*. If this precipitate is dissolved in a saturated aqueous solution of sulphurous acid and the solution heated, the pyrophosphate of lime separates, as the sulphurous acid escapes, in the form of a crystalline crust *b*, which floats on the surface of the liquid at first, but sinks to the bottom as it increases in bulk. Soluble to a small extent in water; insoluble in acetic acid and solution of pyrophosphate of soda. The crystals contain 3 atoms of water. Lime-water is likewise precipitated by pyrophosphoric acid: *c*. The precipitate again dissolves in a large excess of the acid.

| | Calculation. | | Schwarzenberg. | | |
|---|---|---|---|---|---|
| | | | *a.* | *b.* | *c.* |
| 2CaO | 56·0 | 43·96 | 43·77 | 44·68 | 43·59 |
| $bPO^5$ | 71·4 | 56·04 | 56·23 | 55·32 | 56·41 |
| $2CaO, bPO^5$ | 127·4 | 100·00 | 100·00 | 100·00 | 100·00 |

The salt *b* was ignited previous to analysis, (Schwarzenberg, *Ann. Chim. et Pharm.* 65, 2.) ¶

F. Metaphosphate of Lime.—This salt is obtained in the anhydrous state by igniting ordinary monophosphate of lime; it then forms a turbid insoluble glass. Hydrated metaphosphate of lime is precipitated as a clear semifluid mass of the consistence of pitch, by adding metaphosphate of soda to an aqueous solution of chloride of calcium. (Graham, *Pogg.* 32, 70.) A solution of lime in excess of aqueous metaphosphoric acid is not immediately precipitated when supersaturated with ammonia; but after some days, as the metaphosphoric acid changes to the ordinary variety, a gelatinous precipitate is deposited from the mixture. (Liebig, *Ann. Pharm.* 11, 262.)

## Calcium and Sulphur.

A. Monosulphide of Calcium. — 1. By passing sulphuretted *hydrogen gas* over lime ignited in a porcelain tube, water and sulphide

of calcium are produced. (Berzelius, *Schw.* 34, 12.)—2. Dry sulphate of lime is strongly ignited in a charcoal crucible, or mixed with $\frac{1}{3}$ its weight of charcoal: 100 parts of ignited gypsum, heated to whiteness in a charcoal crucible, yield 51·52 parts of sulphide of calcium. (Berthier, *Ann. Chim. Phys.* 22, 233; 24, 275.)—3. Pure lime or its carbonate is ignited with half its weight of sulphur in a close vessel. The *Sulphide of lime, Lime-liver of sulphur, Hepar sulphuris calcareum,* thus obtained, is a mixture of 3 atoms of monosulphide of calcium and 1 atom of sulphate of lime.

$$4CaO + 4S = 3CaS + CaO,SO^3.$$

(*Vid.* Vauquelin, *Ann. Chim. Phys.* 6, 36; Osann, *Kastn. Arch.* 5, 96.) Canton's *Phosphorus* (I., 193) is also a sulphide of calcium.

Sulphide of calcium is white, with a reddish or yellowish tinge, opaque, friable, inodorous, of hepatic taste, and infusible at a white heat. It is scarcely altered by being roasted in the fire. (Berthier.) When boiled with large quantities of water frequently renewed, it is slowly converted into a solution of double sulphide of hydrogen and calcium (bihydrosulphate of lime), and hydrate of lime which remains undissolved; a portion of sulphide of calcium still continuing mixed with it. (H. Rose, *Pogg.* 55, 433.)

| | | Calculation. | |
|---|---|---|---|
| Ca | 20 | ..... | 55·55 |
| S | 16 | ..... | 44·44 |
| CaS | 36 | ..... | 100·00 |

*Hydrated Monosulphide of calcium,* or *Mono-hydrosulphate of lime,* appears, according to H. Rose, to have no existence.

B. Hydrated Sulphide of Hydrogen and Calcium, or Bi-hydrosulphate of Lime.—1. Sulphuretted hydrogen gas is passed into water in which hydrate of lime or sulphide of calcium is diffused, as long as it continues to be absorbed. It is only by using a large quantity of water that the whole of the hydrate of lime or the sulphide of calcium can be converted into this soluble compound; when the quantity of water is too small, sulphide of calcium remains undissolved. However long, therefore, sulphuretted hydrogen may be passed through hydrate of lime, nothing is obtained but sulphide of calcium, together with a small quantity of bihydrosulphate of lime which dissolves in the water set free from the hydrate of lime. For the same reason, the aqueous solutions of chloride of calcium and the double sulphide of hydrogen and potassium, when mixed in a concentrated state, give a slimy precipitate, with abundant evolution of sulphuretted hydrogen; whereas, the same solutions when diluted yield no precipitate whatever; because, in this case, a solution of double sulphide of hydrogen and calcium is produced (bihydrosulphate of lime). (Berzelius.) Moistened hydrate of lime alone does not absorb sulphuretted hydrogen gas with near so much rapidity as when mixed with sulphate of soda; because, in the latter case, sulphate of lime and bi-hydrosulphate of soda are formed, the latter of which can exist when only a small quantity of water is present. (Graham, *Phil. Mag. J.* 18, 519.)—2. Sulphide of calcium is repeatedly boiled with water, and filtered. The colourless solution has a sharp, bitter, hepatic taste, and a slightly corrosive, alkaline reaction.

The solution evaporated in vacuo or in an atmosphere of hydrogen gas, evolves sulphuretted hydrogen; deposits needles; and when near dry-

ness, swells up, with rapid evolution of sulphuretted hydrogen, and leaves sulphide of calcium. (Berzelius, *Pogg.* 6, 442.) The solution evaporated in a retort containing air, suffers a large quantity of sulphuretted hydrogen to escape with the steam; deposits sulphate of lime in the form of a white powder on further concentration; and when still further evaporated and cooled, yields orange-coloured needles of the compound D, while the mother-liquid still retains bi-hydrosulphate of lime. The hyposulphite of lime produced by contact of air imparts sulphur to a portion of the sulphide of calcium, and is itself converted into sulphite; and the pentasulphide of calcium thus formed, produces the yellow needles by combining with lime which has lost its sulphuretted hydrogen. (H. Rose.)

C. Pentasulphide of Calcium and Hydrosulphite of Lime.—Monosulphide of calcium ignited with sulphur does not take up any portion of that substance. (Berzelius.) One part of monosulphide of calcium or of hydrate of lime is diffused in water, boiled for a long time with sulphur, and filtered. When hydrate of lime is used, the solution likewise contains hyposulphite of lime (II., 193, 4); and if the lime is in excess, the following compound D is formed, and crystallizes out on cooling. The reddish brown—or, when more diluted, reddish yellow—filtrate, evaporated in vacuo, yields an amorphous, yellow mass, which loses sulphur when heated, and is converted into monosulphide of calcium; it is soluble in water and alcohol. (Berzelius.) Carbonate of ammonia, potash, or soda, precipitates carbonate of lime from the solution, and forms hydrosulphite of ammonia, potash, or soda. [For the behaviour of the aqueous solution on exposure to the air, and with acids, &c., see II., 228.]

D. Hydrated Pentasulphide of Calcium and Lime, or Sex-basic Hydrosulphite of Lime.—Formed: 1. By boiling sulphur with excess of lime and water,

$$13CaO + 12S = 2(5CaO, CaS^5) + CaOS^2O^2.$$

or: $$13CaO + 12S + 2HO = 2(6CaO, HS^5) + CaO, S^2O^2.$$

—2. By boiling the hydrated bi-hydrosulphate of lime in the air, whereupon oxygen gas is absorbed and sulphuretted hydrogen evolved.

$$6(CaS, HS) + HO + 4O = 5CaO, CaS^5 + 7HS.$$

or: $$6(CaO, 2HS) + 4O = 6CaO, HS^5 + 4HO + 7HS.$$

Two parts of lime and one part of sulphur are boiled for a considerable time with water—the filtrate cooled in a close vessel—and the resulting crystals washed with cold water, and dried in vacuo over oil of vitriol. (Herschel, *Ann. Chim. Phys.* 14, 353.)

Orange-coloured, transparent, irregular, six-sided prisms, with irregular trihedral or with dihedral summits. (Bucholz & Brandes, *Schw.* 22, 43.) Four-sided prisms, with dihedral summits; of caustic, bitter, hepatic taste. (Herschel.) Forms a yellow powder, and has an alkaline reaction. (Buchner, *Schw.* 16, 397.) The crystals, when thoroughly dry, remain unaltered in the air. (Herschel.) When moistened, they lose their colour, and are converted into hyposulphite of lime. (Buchner.) Heated out of contact of air, they evolve water and sulphur, without change of form, and leave a white residue, which, when treated with hydrochloric acid, gives off hydrosulphuric acid and deposits sulphur; it also contains sulphate

of lime. (H. Rose, *Pogg.* 55, 433.) Hydrochloric acid decomposes the crystals, yielding hydrosulphuric acid, sulphur, and chloride of calcium. (Buchner, Bucholz, Brandes, Herschel, Rose.) They do not evolve hydrosulphuric acid when mixed with protochloride of manganese. (H. Rose.) Mixed with a large quantity of water, added in successive portions, they leave a residue of hydrate of lime, while pentasulphide of calcium remains in solution (H. Rose); they likewise deposit hydrate of lime when treated with boiling water, but dissolve completely in 400 parts of cold water. (Buchner.) Insoluble in alcohol (soluble, according to Gay-Lussac.)

| | Crystallized. | | | Or: | | | H. Rose. |
|---|---|---|---|---|---|---|---|
| 5CaO | 140 | .... | 33·33 | 6Ca | 120 | .... 28·57 | .... 28·00 |
| $CaS^5$ | 100 | .... | 23·81 | 5O | 40 | .... 9·52 | |
| 20HO | 180 | .... | 42·86 | 5S | 80 | .... 19·05 | .... 18·83 |
| | | | | 20HO | 180 | .... 42·86 | |
| $5CaO, CaS^5 + 20Aq.$ | 420 | .... | 100·00 | | 420 | .... 100·00 | |

| Or: | | | | Herschel. | | Bucholz & Brandes. |
|---|---|---|---|---|---|---|
| 6CaO | 168 | .... | 40·00 | 42·9 | ..... | 42·5 |
| 5S | 80 | .... | 19·05 | 26·0 | ..... | 21·1 |
| H | 1 | .... | 0·24 | 0·6 | ..... | 0·4 |
| 19HO | 171 | .... | 40·71 | 30·5 | ..... | 34·2 |
| $6CaO, HS^5 + 19Aq.$ | 420 | .... | 100·00 | 100·0 | ..... | 98·2 |

E. HYPOSULPHITE OF LIME.—Hydrate of lime is boiled in water with sulphur, and through the filtrate containing hydrosulphite and hyposulphite of lime, sulphurous acid gas is passed till the liquid becomes colourless (Herschel); or the liquid is exposed to the air till it loses its colour. (Gay-Lussac, *Ann. Chim.* 85, 200.) The filtered solution is evaporated at a temperature not exceeding 60°, and then cooled. Large, transparent, colourless six-sided prisms. (Herschel.) The crystals belong to the system discovered by Mitscherlich (I., 16, γ). *Fig.* 120; $a : u = 94° 9'$; $a : u' = 107° 17'$; $a : t = 107° 2'$; $a : m = 98° 21'$; $a : a = 115° 31'$; $a : e = 124° 32\frac{1}{2}'$; $u : u' = 78° 10'$; $t : m = 90°$; &c. (Mitscherlich, *Pogg.* 8, 427.) The crystals effloresce in vacuo over oil of vitriol at ordinary temperatures; but not below 40° in the air. (Herschel.) Heated out of contact of the air, they lose water and sulphur, leaving a mixture of sulphide of calcium and sulphate of lime, probably also mixed with sulphite. (Rammelsberg, *Pogg.* 56, 302.) When a concentrated aqueous solution of the salt is heated above 60°, it is resolved into sulphite of lime and sulphur. From the aqueous solution, carbonate of potash throws down a portion of the carbonate of lime as a glutinous mass; the rest does not separate till the filtrate is heated, or lime-water added; it is then precipitated in the ordinary flakes which soon become granular. One part of the salt is soluble in one part of water at 3°. (Herschel, *Ann. Chim. Phys.* 14, 355; also *Pogg.* 25, 628.)

Crystallized, according to Herschel.

| | | | |
|---|---|---|---|
| CaO | 28 | ..... | 21·54 |
| $S^2O^2$ | 48 | ..... | 36·92 |
| 6HO | 54 | ..... | 41·54 |
| $CaO, S^2O^2 + 6Aq.$ | 130 | ..... | 100·00 |

F. SULPHITE OF LIME.—a. *Monosulphite.*—$CaO, SO^2 + 2Aq.$—At ordinary temperatures, *burnt lime* does not absorb sulphurous acid gas,

—hydrate of lime absorbs it with facility. This salt is precipitated as a white powder on mixing sulphurous acid with lime-water, or sulphite of potash with chloride of calcium; it crystallizes from a solution containing excess of acid—in which it is readily soluble—in six-sided prisms with six-sided summits; tastes slightly hepatic. It contains, according to Fourcroy & Vauquelin, 47 per cent. of lime, 48 of sulphurous acid, and 5 of water. Ignited out of contact of air, it is resolved into a mixture of sulphate of lime and sulphide of calcium. Effloresces in the air, and is converted into sulphate of lime. Soluble in 800 parts of cold water.

b. *Acid-sulphite.*—Prepared by dissolving the neutral salt in aqueous solution of sulphurous acid; or, according to Liebig (*Ann. Pharm.* 17, 72), by saturating an aqueous solution of sulphurous acid with carbonate of lime.

G. Hyposulphate of Lime.—Produced by precipitating the manganese-salt with milk of lime. Coincides in crystalline form, and in the magnitude of its angles, with the strontia-salt; remains unaltered in the air; leaves, after ignition, 50·25 per cent. of sulphate of lime; dissolves in 2·46 parts of water at 19°, and in 0·8 parts of boiling water. Insoluble in alcohol. (Heeren.)

| Crystallized, according to Heeren. | | | |
|---|---|---|---|
| CaO | 28 | ..... | 20·59 |
| $S^2O^5$ | 72 | ..... | 52·94 |
| 4HO | 36 | ..... | 26·47 |
| $CaO, S^2O^5 + 4Aq$ | 136 | ..... | 100·00 |

H. Sulphate of Lime.—Found native in the anhydrous state as *Anhydrite.* Quicklime does not absorb the vapour of anhydrous sulphuric acid at ordinary temperatures, but only at a heat approaching redness. (H. Rose, *Pogg.* 38, 117.) When oil of vitriol is poured upon quicklime, large quantities of material being used, the whole becomes perfectly red hot. (Kastner, *Kastn. Arch.* 16, 229.) Burnt lime on which oil of vitriol or dilute sulphuric acid is dropped, emits light visible in a dark room. (Heinrich.) Calc-spar, limestone, or chalk, either cold or moderately heated, is not decomposed by exposure to the vapour of anhydrous sulphuric acid, or of oil of vitriol: in the latter case however, a thin stratum of sulphate of lime is formed, but it does not increase. (Marx, *N. Br. Arch.* 15, 103.) Sulphate of lime is obtained in the anhydrous state by igniting gypsum. In this state it is called *Burnt Gypsum.*

Anhydrite belongs to the right prismatic system; *Fig.* 70, with an *m*-face between $u^1$ and $u$. $p : u^1$ or $u = 90°$; $t : m = 90°$; $u^1 : u = 100° 8'$; $u^1 : t = 129° 56'$; $u : m = 140° 4'$. Cleavage parallel to $p$, $t$, and $m$. (Hauy.) Ignited gypsum forms a white powder. Specific gravity of anhydrite at 4°, in vacuo = 2·96 (Royer & Dumas); specific gravity of the artificial salt = 2·9271. (Karsten.) Fuses at a strong red heat, and solidifies, on cooling, to a white opaque crystalline mass. Reduced by ignition with charcoal (or with carbonic acid gas; *Leplay & Laurent*) to sulphide of calcium. Not decomposed by fusion with common salt. (Trommsdorff.) [For the decomposition of the aqueous solution by the presence of organic matter, *vid.* II., 191.]

| | | | | | Thomson, | Chene- | Klap- | | Kirwan, | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Crystallized. | | Richter. | Bucholz. | vix. | roth. | Berze- | Berg- | man. | Wen- | zel. |
| CaO ..... | 28 | 41·18 | 44·33 | 43·4 | 43 | 42·43 | 42 | 41 | 40·2 |
| $SO^3$ ..... | 40 | 58·82 | 55·67 | 56·6 | 57 | 57·57 | 58 | 59 | 59·8 |
| $CaO, SO^3$ ... | 68 | 100·00 | 100·00 | 100·0 | 100 | 100·00 | 100 | 100 | 100·0 |

Combinations with water:

α. *Di-hydrated Sulphate of Lime.*—This compound was deposited from the water in a boiler which was working under a pressure of two atmospheres; it formed a greyish granular mass, of specific gravity 2·757, appearing under the microscope in the form of small transparent prisms, coloured with carbonaceous matter. (Johnston, *Phil. Mag. J.* 13, 325; also *J. pr. Chem.* 16, 100.)

| | Calculation. | | Johnston. |
|---|---|---|---|
| $2(CaO, SO^3)$ | 136 .... | 93·79 ..... | 93·272 |
| HO | 9 .... | 6·21 ..... | 6·435 |
| Carbonaceous matter | | | 0·293 |
| $2(CaO, SO^3) + Aq.$ .... | 145 .... | 100·00 ..... | 100·000 |

β. *Bi-hydrated Sulphate of Lime.*—Found as *Gypsum, Marienglas, Fraueneis, Alabaster, Lapis Specularis,* &c. Moderately burned gypsum mixed with water forms a paste at first; but this quickly hardens, heat being evolved, and the water passing into the solid condition of water of crystallization: gypsum burned at too high a temperature, and native anhydrite enter but very slowly into combination with water. The harder the gypsum is before burning, the more solid does it become when subsequently mixed with water. (Gay-Lussac, *Ann. Chim. Phys.* 40, 436.) Artificial gypsum does not solidify so well with water after ignition as the native variety, unless it be previously submitted to powerful pressure while moist, and then dried and ignited. (Payen.) The crystalline system of gypsum is the oblique prismatic (Weiss); *Fig.* 114, and many other forms; $a : a = 36° 7'$; $a : m = 108° 3\frac{1}{3}'$; $u : u^1 = 69° 23\frac{1}{2}'$; $u : m = 124° 41\frac{2}{3}'$; the edge between $a$ and $a : t = 113° 8'$. Cleaves with great ease parallel to $m$; less readily, parallel to $t$ and $i$ (the edge between $a$ and $a$ is truncated; *Hauy*). From an aqueous solution, the hydrated sulphate of lime crystallizes in needles. Specific gravity at 0°, in vacuo = 2·322. (Royer & Dumas.) A solution of the variety known as *Marienglas* in boiling water, and likewise *Marienglas* heated till it exfoliates, turn reddened litmus blue. (Laugier, *J. Chim. Med.* 6, 325; Biewend, *J. pr. Chem.* 23, 252.)

| | Crystallized. | Bucholz, Giese. | Klaproth. | Berthier. | Bergman. |
|---|---|---|---|---|---|
| CaO | 28 .... 32·56 | .... 33 | .... 33·0 | .... 32·8 | .... 32 |
| $SO^3$ | 40 .... 46·51 | .... 46 | .... 45·5 | .... 45·2 | .... 46 |
| 2HO | 18 .... 20·93 | .... 21 | .... 21·5 | .... 22·0 | .... 22 |
| $CaO, SO^3 + 2Aq.$ | 86 .... 100·00 | .... 100 | .... 100·0 | .... 100·0 | .... 100 |

Gypsum loses its water far below a red heat, splitting into layers and crumbling to a white powder. At 100°, in vacuo over oil of vitriol, it parts with half its water; the residue, containing 12·83 per cent. of water, does not solidify when mixed with water. In the air, it begins to lose water just above 100°, and becomes anhydrous at a temperature below 132°. Gypsum deprived of its water at 132° (below 126°, Mitscherlich) solidifies with water; but if the heat rises to 204° (beyond 160°, Mitscherlich) the gypsum becomes over burnt, and solidifies with water as slowly as anhydrite. (Graham, *Phil. Mag. J.* 6, 422.) (For the experiments of Millon and Plessy on the effect of heat on hydrated sulphate of lime, *vid. Liebig & Kopp's Jahresbericht*, 1847–1848, p. 395.) The powder of unburnt gypsum solidifies also when mixed with aqueous solution of potash or of *various salts of potash*, instead of water, hydrated double salts

being probably formed. This effect is produced by solution of potash, by the carbonate and bicarbonate of potash (in the latter case with violent effervescence), by sulphate, bisulphate, and silicate of potash, and by tartrate of potash and soda. On the other hand, chlorate and nitrate of potash and all the salts of soda produce no reaction. The solidification is more rapid than with burnt gypsum and pure water; instantaneous indeed with the tartrate of soda and potash. The solidified mass resembles common hardened gypsum, both in appearance and hardness. A mass of this kind, when reduced to powder, hardens again on being mixed with a fresh solution of some salt of potash. (Emmet, *N. Edinb. Phil. J.* 15, 69; also *J. Pharm.* 19, 685.)

Gypsum dissolves, according to Bucholz, in 460 parts of cold and in the same quantity of hot water; according to Giese, in 380 parts of cold and 388 parts of boiling water. The solution has a weak, faint taste. The solubility of gypsum in water is increased by the presence of sal-ammoniac; but no decomposition is produced by double affinity. (A. Vogel, *J. pr. Chem.* 1, 196.) By the addition of sulphate of soda (O. Henry, *J. Pharm.* 12, 31),—of common salt (the solution in this case not being precipitated by dilute sulphuric acid; Trommsdorff, *N. Tr.* 18, 1, 234; Wackenroder, *Ann. Pharm.* 41, 316),—and of succinate of ammonia (Wittstein, *Repert.* 57, 18).

I. Sulphide of Carbon and Calcium and Hydro-sulphocarbonate of Lime.—By digesting sulphide of calcium with excess of bisulphide of carbon and water, at 30°, in a close vessel, a dark red liquid is obtained; and this, when evaporated in vacuo, yields a mass which is yellowish brown and crystalline at first, but assumes a pale yellow colour when perfectly dry; by exposure to the air, it again changes to brownish yellow from absorption of water. This substance is readily dissolved both by water and alcohol; water however leaves a reddish yellow *basic salt* of a peppery but not hepatic taste; it is always formed when the bisulphide of carbon is not used in excess. The aqueous solution of the neutral salt is decomposed by boiling, with separation of carbonate of lime. (Berzelius.)

## Calcium and Selenium.

A. Monoselenide of Calcium.—1. Aqueous solution of chloride of calcium is precipitated by protoselenide of potassium. Flesh-coloured precipitate.—2. Selenium is heated with lime till the mixture becomes red-hot. There remains in this case a light reddish brown mixture of selenide of calcium and selenite of lime, which assumes a flesh colour when powdered, is destitute of taste and smell, and insoluble in water.—3. The hydrated selenide of hydrogen and calcium preserved in a loosely stopped bottle, deposits [mono?] selenide of calcium in right four-sided prisms of a dark brown colour and opaque. (Berzelius, *Schw.* 23, 443.)

B. Hydrated Selenide of Hydrogen and Calcium or Bi-hydroseleniate of Lime.—Lime-water is saturated with seleniuretted hydrogen, out of contact of air. The air contained in the lime-water causes cloudiness, and subsequently forms a red precipitate. The clear liquid resting above this precipitate acquires a red colour by exposure to the air, commencing at the top, extending downwards, and constantly

increasing in strength, but unaccompanied by turbidity. A film and crystals of selenide of calcium are subsequently deposited, and the liquid again becomes colourless, still retaining a portion of lime in solution. (Berzelius, *Schw.* 23, 465.)

C. Polyselenide of Calcium.—Formed—mixed however with selenite of lime—by heating lime with selenium to a temperature just below the point of ignition. Brownish black, coke-like mass, yielding a reddish brown powder, without taste or smell, and insoluble in water. It is converted by ignition into A, 3, with loss of selenium,—and is decomposed by acids, into lime which dissolves, and red bulky flakes of selenium. No seleniuretted hydrogen is evolved, because it is decomposed by the selenious acid set free at the same time. (Berzelius.)

D. Selenite of Lime.—*a. Monoselenite*—CaO, SeO. Gradually deposited during the solution of carbonate of lime in hydrated selenious acid. Soft, crystalline powder (gritty crystals, *Muspratt*), which fuses at a red heat, and in this state attacks glass powerfully, blistering it in a remarkable manner. Slightly soluble in water. (Berzelius.)

*b. Biselenite.*—Prepared by dissolving *a* in aqueous solution of selenious acid: crystallizes in very small prisms, which are permanent in the air, and lose half their acid by exposure to heat, or by contact with ammonia. (Berzelius, *Schw.* 23, 454.)

## Calcium and Iodine.

A. Protiodide of Calcium.—A solution of lime in aqueous hydriodic acid is evaporated to dryness, and heated out of contact of air. White —tastes like chloride of calcium—fuses below a red heat—and is subsequently decomposed, on the admission of air, into lime and vapour of iodine. It is very soluble in water, and deliquesces when exposed to the air. (Gay-Lussac, *Gilb.* 49, 237.) A solution concentrated by evaporation yields, on cooling, long needles of hydrated iodide of calcium or hydriodate of lime. The solution is colourless, and, when exposed to the air, becomes covered with a film of carbonate of lime. (Berthollet, *J. Pharm*, 13, 416.)

B. Hydrated Periodide of Calcium or Hydriodite of Lime.—A concentrated aqueous solution of iodide of calcium dissolves iodine freely, forming with it, when saturated, a black liquid, which, when evaporated under a bell-jar near a dish containing hydrate or carbonate of potash, yields large, dark grey crystals, having an almost metallic lustre. From a concentrated solution of this substance, hydrate of lime throws down a black, pulverulent, basic compound, which is decomposed by the addition of more water, with separation of iodine. (Berzelius.)

C. Iodide of Lime?—*a.* When vapour of iodine is passed over lime ignited in a porcelain tube, the iodine combines with the lime without liberating oxygen gas. A solution of this substance in water possesses a powerful alkaline reaction. (Gay-Lussac.) When strongly heated, it evolves iodine. (Grouvelle.)

*b.* Hydrate of lime rubbed up in a mortar with excess of iodine, and exposed in vacuo to a temperature of 30° beside a solution of potash, till the excess of iodine has evaporated and been absorbed by the potash,

yields a black mass. This is decomposed by water into a dark brown liquid and a black residue, which, on being washed with water, first becomes blue, and then changes into hydrate of lime. (Berzelius, *Pogg.* 19, 296.)

D. Iodate of Lime.—Crystallizes slowly from the mixed solutions of iodate of potash and chloride of calcium in water (Pleischl); a large quantity of the salt however remains dissolved. (Rammelsberg.) The crystals are rendered anhydrous by heat. The dry salt gently ignited in a porcelain retort evolves 14·785 per cent. of oxygen and 54·072 of iodine, leaving a residue amounting to 31·143 per cent., and consisting chiefly of pentabasic periodate of lime; but when heated more strongly, it evolves a still larger amount of oxygen (in the whole 17·176 per cent.) and of iodine (in the whole 62·478 per cent.), and leaves 20·346 per cent. of a mixture of pentabasic periodate and much free lime, which may be separated by water. (Rammelsberg, *Pogg.* 44, 576.) Iodate of lime detonates violently on ignited charcoal. (Gay-Lussac.) When treated with concentrated hydrochloric acid, by which it is readily dissolved, it yields an orange-coloured liquid, smelling of terchloride of iodine, and similar to that yielded by iodate of potash; it does not however yield crystals of the double chloride of iodine and calcium. (Filhol.)

*Hydrated Iodate of Lime.*—Four-sided prisms, or in powder. The crystals effloresce in the air, with partial loss of water, and become anhydrous at a temperature below 200°. (Rammelsberg.) They dissolve in 454 parts of water at 18°, and in 102 parts of boiling water (Gay-Lussac); in 253 parts at 15°; in 75 parts of boiling water; and much more abundantly in nitric acid. From the latter solution, the salt is precipitated in prisms by ammonia. (Rammelsberg.) Alcohol separates the salt from an aqueous solution. (O. Henry.)

| | Anhydrous. | | | | Crystallized. | | | Rammelsberg. |
|---|---|---|---|---|---|---|---|---|
| CaO | 28 | .... | 14·43 | CaO | 28 | .... | 11·71 | .... 12·57 |
| $IO^5$ | 166 | .... | 85·57 | $IO^5$ | 166 | .... | 69·46 | .... 68·60 |
| | | | | 5HO | 45 | .... | 18·83 | .... 18·83 |
| CaO, $IO^5$ | 194 | .... | 100·00 | CaO, $IO^5$ + 5Aq. | 239 | .... | 100·00 | .... 100·00 |

E. Periodate of Lime.—*a. Pentabasic salt.* Remains after the ignition of iodate of lime in a retort, and is purified from the free lime mixed with it, by digestion in water. (Rammelsberg.)

*b.* From a neutral mixture of hyperiodic acid and soda, chloride of calcium sets a portion of acid free, and precipitates a white basic salt easily soluble in dilute nitric acid. (Benckiser, *Ann. Pharm.* 17, 259.)

## Calcium and Bromine.

A. Bromide of Calcium.—1. A solution of lime or of carbonate of lime in aqueous hydrobromic acid is evaporated to dryness and heated. (Löwig.)—2. An aqueous solution of bromide of iron is decomposed by lime; boiled in the air till the green precipitate assumes a brick-red colour; then filtered, evaporated to dryness, and heated. (O. Henry, *J. Pharm.* 15, 52.)—3. Lime is ignited in vapour of bromine. (Löwig.)—White substance, having a sharp bitter taste. (Löwig.) Fuses at a full red heat to a white mass, emitting at the same time an odour of bromine, in consequence of partial decomposition. With oil of vitriol it evolves

hydrobromic acid at first, then bromine and sulphurous acid. (O. Henry.) It evolves heat by contact with water, and deliquesces rapidly in the air. (Löwig.) Very soluble in alcohol. (O. Henry.)

| | | Calculation. | |
|---|---|---|---|
| Ca | 20·0 | ..... | 20·33 |
| Br | 78·4 | ..... | 79·67 |
| Ca Br | 98·4 | ..... | 100·00 |

*Hydrated Bromide of Calcium*, or *Hydrobromate of Lime.*—From a solution of bromide of calcium, colourless silky needles are obtained, but with difficulty. (O. Henry, Berthemot.)

B. Hydrated Bromide of Calcium and Lime or Basic Hydrobromate of Lime.—By boiling bromide of calcium with milk of lime, filtering, and then allowing the solution to cool, delicate needles are obtained, resembling the tetrabasic hydrochlorate of lime, and decomposed by water into bromide of calcium, which dissolves, and an insoluble residue of lime. (Löwig.)

An aqueous solution of bromide of calcium may be made to take up more bromine, but evolves it again when evaporated in a close vessel over hydrate of potash. (Berzelius.)

C. Hypobromite of Lime?—An intimate mixture of hydrate of lime with a large quantity of bromine, deprived of the excess of bromine by evaporation in vacuo over hydrate of potash, leaves a dry, inodorous mass of a light cinnabar colour—probably a mixture of hypobromite of lime and perbromide of calcium.—The mass becomes yellow on the addition of water, and partly dissolves, forming a yellow bleaching liquid, which deposits carbonate of lime on exposure to the air. The insoluble portion, treated with more water, continually becomes of a paler yellow, and at last leaves nothing but white hydrate of lime: the solution then contains bromate of lime together with the compound B. (Berzelius, *Pogg.* 16, 405; 19, 295.)—Balard (*J. pr. Chem.* 4, 165) has obtained the same compound. The cinnabar-coloured mass when exposed to the air, emits an odour of bromine, and deliquesces—with separation of hydrate of lime—to a yellow, powerfully bleaching liquid, which may be preserved in close vessels. A similar solution also may be prepared with bromine and milk of lime; when evaporated in vacuo, it yields the same red-coloured mass. (Balard.)

Bromine does not act on quicklime or carbonate of lime, but only on the hydrate. Milk of lime mixed with bromine produces a yellow bleaching liquid. This, when heated, evolves bromine, followed by oxygen gas, and leaves bromide of calcium or hydrobromate of lime. All acids, even carbonic acid, expel the bromine. The liquid oxidizes many of the metals, and gives with nitrate of silver a white precipitate which rapidly changes to black, and is composed of a mixture of oxide, bromide, and bromate of silver: the bleaching power is at the same time destroyed. But if the milk of lime is mixed with bromine in excess, so that it smells slightly of that substance, it yields, with a silver salt, a white precipitate of bromide of silver containing very little bromate, and retains its bleaching power: this power, however, gradually disappears, the change being attended with slow evolution of oxygen gas and separation of bromide of silver. (Löwig.)

D. Bromate of Lime.—Prepared by saturating an aqueous solution of bromic acid with lime (Löwig) or carbonate of lime (Rammelsberg). It crystallizes in combination with water in large flat tables, having a sharp bitter taste (Löwig); in small, sharply acuminated prisms (Rammelsberg).—The crystals do not lose water in vacuo at ordinary temperatures, or in the air below 100°; they do not become anhydrous till heated to 180°. The anhydrous salt is decomposed by ignition into oxygen gas and bromide of calcium, which remains in the form of a loose white mass. (Rammelsberg.) The salt detonates on ignited charcoal. (Löwig.) It is soluble in 1·1 part of cold water; the saturated solution is of a syrupy consistence. (Rammelsberg, *Pogg.* 52, 88.)

| | Anhydrous. | | |
|---|---|---|---|
| CaO | 28·0 | | 19·12 |
| $BrO^5$ | 118·4 | | 80·88 |
| $CaO, BrO^5$ | 146·4 | | 100·00 |

| | Crystallized. | | Rammelsberg. |
|---|---|---|---|
| CaO | 28·0 | 18·02 | 18·092 |
| $BrO^5$ | 118·4 | 76·19 | 75·939 |
| HO | 9·0 | 5·79 | 5·969 |
| $CaO, BrO^5 + Aq$ | 155·4 | 100·00 | 100·000 |

## Calcium and Chlorine.

A. Chloride of Calcium.—Found in many springs.—Lime heated in chlorine gas absorbs it, and evolves half a measure of oxygen gas.—Lime heated in hydrochloric acid gas absorbs it rapidly, with evolution of heat but not of light, and formation of water. (Chevreul.)—At a white heat, also, lime forms chloride of calcium with hydrochloric acid gas; and with a mixture of equal volumes of hydrochloric acid gas and carbonic acid gas, chloride of calcium and carbonate of lime are produced. (Petzholdt.) Lime, on which aqueous hydrochloric acid is dropped, emits light visible in a dark room. (Heinrich.)—Chloride of calcium rendered anhydrous by heat is white, opaque, and porous; but after fusion forms a dense, transparent mass, of crystalline granular texture; specific gravity about 2·0401 (Karsten); 2·214 to 2·269 (Pol. Boullay). Fuses at a strong red heat (Dulong); is rendered phosphorescent by irradiation (*Homberg's Phosphorus*); a non-conductor of electricity (H. Davy); has a rough, bitter taste.

By ignition in the air, a small portion of the chloride of calcium is converted into lime, so that the solution has an alkaline reaction. (Liebig.) The longer it is ignited, especially if frequently moistened with water, the larger is the quantity of lime left behind on subsequently dissolving it in water. If it be fused in a platinum crucible, the lime produced attacks the platinum strongly, and the mass acquires a brownish grey colour. (E. Kraus, *Pogg.* 43, 138.)—If carbonic acid gas is passed for an hour and a half into a crucible containing chloride of calcium kept at a white heat and stirred up with a rod of pipe-clay, a dark-brown mass is obtained, from which water extracts chloride of calcium and a small quantity of caustic lime,—while light-brown flakes, consisting of carbonate of lime, platinum, and a little silica from the pipe-clay, remain undissolved. (Petzholdt, *J. pr. Chem.* 17, 464.)—Chloride of calcium, *treated with oil of* vitriol, gives off hydrochloric acid gas. Distilled with

aqueous acetic acid, it yields more or less hydrochloric acid, with formation of acetate of lime. (Buchner, *Repert.* 14, 489.)

| | Calculation. | | | Ure. | | Döbereiner. |
|---|---|---|---|---|---|---|
| Ca | 20·0 | .... | 36·1 | 36·7 | ..... | 38·46 |
| Cl | 35·4 | .... | 63·9 | 63·3 | ..... | 61·54 |
| Ca, Cl | 55·4 | .... | 100·0 | 100·0 | ..... | 100·00 |

| | Calculation. | | | Berzelius. | Marcet. | Wenzel. | Berthollet. |
|---|---|---|---|---|---|---|---|
| CaO | 28·0 | .... | 50·54 | 51·117 | 50·77 | 49 | 42·7 |
| $MuO^2$ | 27·4 | .... | 49·46 | 48·883 | 49·23 | 51 | 57·3 |
| CaO, $MuO^2$ | 55·4 | .... | 100·00 | 100·000 | 100·00 | 100 | 100·0 |

*Sex-hydrated Chloride of Calcium* or *Penta-hydrated Hydrochlorate of Lime.—Fixed sal-ammoniac, Sal-ammoniacum fixum.*—Chloride of calcium combines with water, the combination being attended with evolution of heat. It absorbs water greedily from other substances, especially the gases, and deliquesces rapidly in the air. Chloride of calcium is obtained as a by-product in the preparation of caustic ammonia and carbonate of ammonia; in an impure state, also, from the mother-liquor of many salt-springs. A highly concentrated, hot solution yields crystals on cooling. Regular six-sided prisms, often striated (as *Fig.* 146, but with the *p*-face); $r : \sigma = 120°$ to 121° or nearly so. The crystals melt considerably below 100°.—If kept for twelve days in vacuo in the summer time, they part with 4 atoms of water and become opaque, but do not fall to pieces: after this change, they resemble talc, and retain only 2 atoms of water, CaCl, 2HO. (Graham, *Ann. Pharm.* 29, 31.) At 200° they fuse and part with 4 atoms of water, leaving a white porous mass. (Mitscherlich.) They effloresce when placed over oil of vitriol under the evaporating receiver. (Bonsdorff.)—Heated above the melting point, but still below ignition, the compound swells up strongly and gives off the whole of its water.

| Crystallized Chloride of Calcium. | | | | Berzelius. |
|---|---|---|---|---|
| CaCl | 55·4 | .... | 50·64 | 50·397 |
| 6HO | 54·0 | .... | 49·36 | 49·603 |
| CaCl + 6Aq. | 109·4 | .... | 100·00 | 100·000 |
| Or: | | | | |
| CaO | 28·0 | ..... | 25·60 | |
| HCl | 36·4 | ..... | 33·27 | |
| 5HO | 45·0 | ..... | 41·13 | |
| CaO, HCl + 5Aq. | 109·4 | ..... | 100·00 | |

CaCl + 6Aq corresponds to the most highly concentrated hydrochloric acid (II., 324) = HCl + 6Aq. (Kane.)

Anhydrous chloride of calcium dissolves in water with evolution of heat; the crystallized salt, with production of cold; but both deliquesce rapidly in the air. 100 parts of chloride of calcium in powder exposed to an atmosphere saturated with moisture, absorb 124 parts of water in 96 days; much more, therefore, than is required for complete deliquescence. (Brandes, *Schw.* 51, 433.)—Crystallized chloride of calcium dissolves in half its weight of water at 0°, in one-fourth of its weight at 16°, and in every proportion of hot water. Both dry and hydrated chloride of calcium are readily soluble in alcohol.

*Strength of an Aqueous Solution of Chloride of Calcium, according Richter.* (*Stöchiom.* 3, 171.)

| Sp. gr. | Per cent. | Sp. gr. | Per cent. | Sp. gr. | Per cent. | Sp. gr. | Pe |
|---|---|---|---|---|---|---|---|
| 1·45 | 41·91 | 1·33 | 34·57 | 1·21 | 23·93 | 1·09 | 1 |
| 1·42 | 40·43 | 1·30 | 32·35 | 1·18 | 20·85 | 1·06 | |
| 1·39 | 38·31 | 1·27 | 29·67 | 1·15 | 17·60 | 1·03 | |
| 1·36 | 36·49 | 1·24 | 26·86 | 1·12 | 14·42 | | |

B. Hydrated Chloride of Calcium and Lime or Hydra Tetra-hydrochlorate of Lime.—Noticed by Bucholz and Trom dorff, also by Berthollet, (*Stat. Chim.* 1, 350), and more particularly amined by H. Rose, (*Schw.* 29, 155.) When chloride of calcium is bo with hydrate of lime in a small quantity of water, or when the resi obtained in the preparation of liquid ammonia is exhausted with a sm quantity of water and filtered hot, this compound crystallizes out in l slender needles as the solution cools. These crystals are resolved by wa or alcohol into chloride of calcium which dissolves, and hydrate of l which remains undissolved; water, however, takes up a small portion lime together with the chloride. The carbonic acid of the air converts crystals into a mixture of carbonate of lime and hydrated chloride of cium. (H. Rose, *vid.* also Palm, *Taschenb.* 1821, 167.)

| | Crystallized. | | Or: | | | H. |
|---|---|---|---|---|---|---|
| 3CaO | 84·0 | 29·64 | 4CaO | 112·0 | 39·52 | 41 |
| CaCl | 55·4 | 19·55 | $MuO^2$ | 27·4 | 9·67 | 9 |
| 16HO | 144·0 | 50·81 | 16HO | 144·0 | 50·81 | 49 |
| 3CaO, CaCl + 16Aq. | 283·4 | 100·00 | | 283·4 | 100·00 | 100 |

C. Hypochlorite of Lime.—Known only in a state of mixt with chloride of calcium in equivalent proportions, forming the compo called *Chloride of Lime.*

*a. Chloride of Lime in Powder.—Formation.*—Chlorine gas is absorbed by quicklime or by carbonate of lime. Hydrate of lime milk of lime absorb it rapidly, with rise of temperature, and nearly atomic proportions.

$$2CaO + 2Cl = CaCl + CaO, ClO.$$

In saturating dry hydrate of lime with chlorine gas, Weiss obser an emission of light. (*Kastn. Arch.* 25, 182.) By saturating hydrat lime rapidly with chlorine gas, its temperature may be raised to 1 (Morin.) One atom of lime slaked with only $\frac{1}{2}$ At. water abs but $\frac{1}{2}$ atom of chlorine; slaked with from 1 to 2 atoms of water, howe it absorbs $\frac{1}{2}$ At. chlorine. (Morin.) According to Welter and Dal one atom of hydrate of lime never absorbs more than $\frac{1}{2}$ At. chlor This, however, is to be explained by the fact that lime slaked in ordinary way is generally mixed with portions of quicklime, and on account cannot be perfectly saturated with chlorine. Lime slaked w a large quantity of water—the excess of which is afterwards driven of a heat a little above the boiling point—absorbs chlorine nearly in proportion of one atom of chlorine to one atom of lime (53 parts of c rine to 47 parts of lime.) (Houton-Labillardière.) According to Ure, parts of lime exposed in the state of hydrate to chlorine gas, absorb fi 24 to 28 parts, or not quite one atom, though much more than half an a *of chlorine.* If the chlorine is passed at first in too great quantity o

the hydrate of lime, absorption takes place so rapidly that the temperature rises very considerably. Even if the heat evolved reaches only 30° or from that temperature to 119° (86° to 246·2° F.), the lime absorbs the same quantity of chlorine gas as in the cold, but is found to possess only two-thirds of the bleaching power. Hence a temperature between 30° and 119° causes the change of $\frac{1}{3}$ of the chloride of lime (or hypochlorite of lime) into chloride of calcium and chlorate of lime; this change occurs without any escape of oxygen gas. (Morin.) According to E. Dingler, oxygen gas is evolved when the absorption is attended with evolution of heat.

*Preparation.* Well slaked lime is saturated with chlorine gas, rise of temperature being carefully avoided. On the large scale, the lime is slaked by immersing sieves filled with it in water and withdrawing them again immediately, whereupon the lime crumbles to powder. By this treatment, however, the lime is but imperfectly slaked, and contains too little water: it should therefore be slaked with a large quantity of water, and brought to the consistence of cream, and the excess of water afterwards expelled by heat. (Houton-Labillardière.) An excess of water in the hydrate of lime renders the absorption more difficult. (Dingler.) The chlorine gas must be slowly passed into the hydrate of lime at the commencement,—otherwise the temperature will rise and the bleaching power will be weakened. Labarraque (*J. Chim. Med.* 2, 165), mixes the moistened hydrate of lime with $\frac{1}{10}$ of its weight of common salt, by which means the absorption is greatly facilitated.

On the large scale, the chlorine is prepared from peroxide of manganese and hydrochloric acid (or peroxide of manganese, common salt, and sulphuric acid) in vessels of cast iron, lead, glass, or earthenware, heated by steam or in a sand bath. The gas is passed through a leaden tube into a leaden vessel containing water, where the impurities are deposited, and then into the hydrate of lime. The lime is placed in thin layers either on the stone floor of a chamber built of sandstone or brick, and occasionally stirred about; or on several shelves or dishes arranged in a chamber one above the other; or it is put into vessels connected by tubes through which the chlorine is admitted and carried off.

Chloride of lime must be preserved in well closed vessels, kept cool and away from the light.

It is a white powder, usually moist, and smelling slightly of hypochlorous acid.

| | Calculation. | | Ure. | Houton. |
|---|---|---|---|---|
| CaO | 28·0 | 38·68 | 43 | 47 |
| HO | 9·0 | 12·43 | 17 | |
| Cl | 35·4 | 48·89 | 40 | 53 |
| CaO, HO + Cl | 72·4 | 100·00 | 100 | 100 |

Or:

| | | |
|---|---|---|
| CaCl | 55·4 | 38·26 |
| CaO, ClO | 71·4 | 49·31 |
| 2HO | 18·0 | 12·43 |
| CaCl + CaO, ClO + 2Aq. | 144·8 | 100·00 |

Every specimen of chloride of lime, whether prepared on the large or the small scale, contains less chlorine than the calculated quantity; because either more or less of the lime always remains uncombined:

perfect saturation with chlorine would probably even interfere with the bleaching properties. Houton-Labillardière estimated the amount of chlorine too high.

Chloride of lime is changed by heat into a mixture of chloride of calcium and chlorate of lime, with evolution of oxygen and sometimes also of chlorine gas; at the same time, it loses its bleaching powers. Whether chloride of lime possesses its full bleaching power = 100°, or from rise of temperature during the absorption of the chlorine, one-third of that power is lost, and 67° only remains,—it still evolves, when strongly heated, the same amount of oxygen gas. An evolution of chlorine sometimes precedes that of the oxygen, if the heat be very gradually increased (especially when the lime is saturated as completely as possible with chlorine; *Ure.*) 18 atoms of chloride of lime are resolved in this manner into 12 atoms of oxygen, 17 atoms of chloride of calcium, and one atom of chlorate of lime. (Morin.)

$$9CaCl + 9(CaO, ClO) = 12O + 17CaCl + CaO, ClO^5.$$

At a lower temperature, therefore, $\frac{1}{3}$ of the hypochlorite of lime is resolved into chloride of calcium and chlorate of lime, the other $\frac{2}{3}$ remaining unchanged; and the residue, if afterwards more strongly heated, is no longer decomposed in the same manner, but resolved into oxygen gas and chloride of calcium. (Morin.) [The cause of this reaction is yet to be explained.] Bleaching powder exposed to the air soon attracts moisture, and finally deliquesces, slowly evolving oxygen gas, and forming a liquid which no longer bleaches, and contains chloride of calcium. (Morin.) [The other decompositions will be given under *Solution of chloride of lime.*]

*b. Solution of Chloride of Lime.—Bleaching Liquid.*—1. Powdered chloride of lime is treated with water; and the solution, which contains a small quantity of free lime besides the chloride, is separated by decantation from the insoluble residue. Chloride of lime, shaken up with half its weight of water, yields a filtrate containing 4 per cent. of chlorine; the first, second, and third washings yield solutions of the same strength; but afterwards the filtrate becomes poorer in chlorine. If the chloride of lime contained chloride of calcium ready formed, the first extract would be much richer in chlorine. (Dingler.)—2. Chlorine gas is passed through milk of lime nearly to saturation, and the liquid decanted from the excess of lime. An excess of chlorine would cause a partial formation of chlorate of lime, and lessen the bleaching power. Chlorine water does not act on carbonate of lime.

Transparent and colourless liquid, having a slight odour of hypochlorous acid, and an astringent taste. [The liquid kept in large vessels at the well conducted manufactory of Kestner at Than, exhibits a bright blue colour by reflected light. Does this colour properly belong to the aqueous solution of choride of lime?]

The solution, when boiled, evolves pure oxygen gas, loses its bleaching power, and afterwards contains a mixture of one atom of chlorate of lime with 17 atoms of chloride of calcium. (Morin.) This decomposition is the same as that which takes place with the powdered chloride of lime. It is immaterial whether the solution obtained from the chloride of lime prepared in the cold, and having a bleaching power = 100°, be employed, or that from the chloride formed at a higher temperature, and having a *bleaching power* of 67°. Both evolve the same quantity of oxygen gas, *and yield the same* quantities of chlorate of lime and chloride of calcium;

the latter variety contains the same proportion of chlorate of lime before being heated, as after the expulsion of the oxygen gas. Consequently, in the solution of chloride of lime of 100° bleaching power, two changes occur simultaneously on the application of heat—namely, that of one-third of the compound into chloride of calcium and chlorate of lime,—and that of the other two-thirds into chloride of calcium and oxygen gas; whereas, in the solution of chloride of lime of 67° bleaching power, the latter change only takes place. (Morin.) Even in close vessels at ordinary temperatures the liquid slowly evolves oxygen gas, especially if exposed to light, and finally there remains a solution of chloride of calcium quite destitute of bleaching properties. (Grouvelle, Morin.)

If the chloride of lime, previously to being dissolved, has lost a third of its bleaching power from evolution of heat during the absorption of the chlorine, the decomposed liquid contains chlorate of lime as well as chloride of calcium. (Morin.) Exposed to the direct rays of the sun, the hypochlorite of lime is converted into chlorite, $CaO, ClO^3$. (Gay-Lussac, *Ann. Pharm.* 39, 124.) Acids, including even the carbonic, convert chloride of lime into a lime-salt and free chlorine.

$$CaCl + CaO, ClO + 2SO^3 = 2(CaO, SO^3) + 2Cl.$$

If added in insufficient quantity, they also give rise to the evolution of hypochlorous acid. Carbonic acid gas passed through bleaching liquid, destroys its bleaching powers, expelling chlorine gas and precipitating carbonate of lime; a small quantity of chloride of calcium only remains dissolved, together with acid carbonate of lime. Atmospheric air acts in a similar manner, but more slowly; but if previously freed from its carbonic acid by being passed through potash, it produces no change whatever. (Gaultier de Claubry.) In the open air, the liquid gradually evolves chlorine gas, and becomes covered with a crust of carbonate of lime; if this film be broken up from time to time, the conversion into carbonate of lime and chlorine is completely accomplished in the course of a week. But when the crust is allowed to remain, the liquid is slowly resolved, as in close vessels, into oxygen gas (free from chlorine) and chloride of calcium—a circumstance which must be attended to when the liquid is to be used for disinfecting purposes. (Morin.) Bleaching liquid destroys organic colours and the odour of decomposing organic matter, but only in the presence of an acid which sets chlorine free. Tincture of litmus is not immediately decolorized by bleaching liquid, but only after some time, by the action of the carbonic acid in the air; the effect is accelerated by blowing the air from the lungs through the liquid. (Gmelin.) If air is first blown through putrid blood, and then through bleaching liquid, it precipitates carbonate of lime from the latter and loses its bad odour; if, however, it be passed, first through putrid blood, then through potash or milk of lime—which absorb the carbonic acid—and lastly through bleaching liquid, it retains the bad odour. (Gaultier de Claubry, *Ann. Chim. Phys.* 33, 271.) Carbonate of potash precipitates carbonate of lime from bleaching liquid, producing aqueous chloride of potash. If the bleaching liquid is obtained by dissolving chloride of lime of 67° strength, the chlorate of lime which it contains is converted into chlorate of potash, and in this form may be quantitatively estimated. (Morin.) [For a further account of the properties of chloride of lime, *vid.* II., 301—304.]

On Chloride of Lime *vide* Dalton, (*Ann. Phil.* 1, 15; 2, 6; also *Schw.* 10, 445; 11, 36; further, *Phil. Mag.* 65, 126.—Welter, *Ann. Chim. Phys.*

7, 383; also *N. Tr.* 3, 1, 244.—Thomson, *Ann. Phil.* 13, 182; also *N. Tr.* 4, 2, 76; and further, *Ann. Phil.* 15, 401.—Grouvelle, *Ann. Chim. Phys.* 17, 37.—Ure, *Quart. J. of Sc.* 13, 1; also *Schw.* 35, 183.—Gay-Lussac, *Ann. Chim. Phys.* 26, 163; also *Repert.* 19, 424.—Houton-Labillardière, *J. Chim. Med.* 1, 501.—Chevallier, *J. Chim. Med.* 2, 173.—Morin, *Ann. Chim. Phys.* 37, 139; abstr. *J. Pharm.* 14, 336.—Marezeau, *Pogg.* 22, 273.—E. Dingler, *Kastn. Arch.* 18, 252.)

D. Chlorate of Lime.—Formed on heating the chloride of lime. An aqueous solution of chloric acid is saturated with lime, and evaporated to the crystallizing point. The salt crystallizes in rhomboidal prisms. (Wächter.) The crystals melt in their own water of crystallization when gently heated, and are decomposed in the same manner as the baryta salt (Wächter); they contain 28·3 per cent. of lime, 55·2 of chloric acid, and 16·5 of water = $CaO\,ClO^5 + 2Aq.$; detonate slightly on ignited charcoal; deliquesce in the air; and dissolve readily in water and alcohol. (Chenevix.) From an aqueous solution, iodic acid precipitates iodate of lime. (Serullas, *Ann. Chim. Phys.* 45, 281.)

E. Perchlorate of Lime.—The solution evaporated to a syrupy consistence, solidifies on cooling and forms a mass which rapidly deliquesces when exposed to the air, even in a drying-chamber: its alcoholic solution burns with a reddish flame. (Serullas, *Ann. Chim. Phys.* 46, 304.)

## Calcium and Fluorine.

A. Fluoride of Calcium.—Found in the mineral kingdom as *Fluor-spar;* also in animal bodies, and in some mineral waters.—On mixing the aqueous solution of a lime-salt with aqueous solution of hydrofluoric acid, fluoride of calcium is obtained in the form of a translucent gelatinous precipitate, which has a reddish opalescent lustre, stops up the filter, and cannot be washed; by the addition of ammonia, however, it is rendered somewhat more compact. On the contrary, by treating freshly precipitated carbonate of lime with aqueous hydrofluoric acid, the fluoride of calcium is obtained as a granular powder, which may be easily washed. From the concentrated solution of any lime-salt, hydrofluoric acid throws down fluoride of calcium, in light flakes; in very dilute or highly acid solutions of lime, the precipitate is not produced without the addition of ammonia. (Berzelius, *Pogg.* 1, 20.) Fluor-spar belongs to the regular system of crystallization; *Fig.* 1, 2, 3, 4, 5, 6, 8, 9. Cleavage distinct, parallel to the $\sigma$-surface. Specific gravity, from 3·14 to 3·177. It decrepitates when heated, and fuses at 51° Wedgwood. (Saussure.) Fuses in a porcelain furnace, and on cooling solidifies to a crystalline mass of different density, and having the cleavage-planes of the octohedron. (Magnus, *Pogg.* 20, 482.) Becomes phosphorescent by insolation and by heat. Tasteless. Permanent in the air.

| | Calculation. | | H. Davy. |
|---|---|---|---|
| Ca ..... | 20·0 .... | 52·68 .... | 53·313 |
| F ..... | 18·7 .... | 47·32 .... | 46·687 |
| CaF ..... | 38·7 .... | 100·00 .... | 100·000 |

| Or: | Calculation. | | Berzelius. | Sir H. Davy. |
|---|---|---|---|---|
| Lime | 28·0 | 72·35 | 72·6855 | 72·7 |
| Hyp. Anhyd. Fluoric Acid | 10·7 | 27·65 | 27·3145 | 27·3 |
| Hyp. Anhyd. Fluoride of Calcium .... | 38·7 | 100·00 | 100·0000 | 100·0 |

| Klaproth. | Thomson. | Richter. | Dalton. |
|---|---|---|---|
| 67·75 | 65·7 | 65 | 60 |
| 32·25 | 34·3 | 35 | 40 |
| 100·00 | 100·0 | 100 | 100 |

Fluor-spar fuses readily when first heated by the blowpipe; but by prolonged ignition, it gradually loses hydrofluoric acid and is changed into a blistered infusible mass of pure lime. (Smithson, *Ann. Phil.* 23, 101.) It is not decomposed by boiling with a solution of potash or soda, or by fusion with their hydrates; but when it is fused in a finely divided state, with carbonate of potash or soda, carbonate of lime and fluoride of potassium or sodium are produced. (Berzelius.) The decomposition is only partial. (Berthier, Gmelin.) The vapour of anhydrous sulphuric acid does not affect fluor-spar at a red heat; that of oil of vitriol, however, decomposes it very easily. (Kuhlmann, *Berz. Jahresbericht*, 8, 86.) 100 parts of fluor-spar ignited with oil of vitriol, leave 175 parts of sulphate of lime. (Berzelius.) With cold oil of vitriol, fluor-spar yields a clear ropy liquid (if it contain silica, however, it effervesces, and does not yield a transparent fluid, on account of the formation of gypsum): decomposition commences at 40°, and the transparency is destroyed. Water separates the fluor-spar from the cold solution. Concentrated hydrochloric and nitric acids behave in a similar manner, only they do not produce so viscid a liquid. Boiling nitric acid decomposes fluoride of calcium partially. Boiling dilute hydrochloric acid dissolves a small quantity, which is again precipitated by alkalis, and likewise remains behind when this liquid is evaporated. When silica is present in the fluor-spar, nitric and hydrochloric acids dissolve a larger quantity, in the form of fluoride of silicium and calcium. Aqueous hydrofluoric acid takes up but a very small quantity of fluor-spar. It does not evolve heat with this acid, unless it contains silica. (Berzelius.) Insoluble in water.

B. Hydrated Fluoboride of Calcium, or Hydrofluate of Borate of Lime.—Obtained by the spontaneous evaporation of a solution of carbonate of lime in tetra-hydrofluate of boracic acid (the lime not being in excess), or of a solution of artificially prepared fluoride of calcium in ter-hydrofluate of boracic acid. It forms a gelatinous precipitate, having an acid taste and reddening litmus. Water—especially when hot—decomposes this compound, dissolving out an *acid* salt, and leaving a *basic* salt which contains fluoride of calcium in excess. (Berzelius.)

## Calcium and Nitrogen.

A. Nitrite of Lime.—Prepared like nitrite of baryta, by the first method. ¶ Or more readily by treating a boiling aqueous solution of nitrite of silver with lime-water—passing sulphuretted hydrogen through the clear liquid, if the silver salt is in excess, or carbonic acid gas if the lime predominates—and evaporating to the crystallizing point. Prismatic

crystals insoluble in dilute alcohol. (Fischer, *Pogg.* 74, 115.) ¶ It exhibits the same properties as the nitrate, deliquescing with the same rapidity. Contains 27·345 per cent. of lime. (Hess, *Pogg.* 12, 260.)

B. Nitrate of Lime.—*a. Basic.*—A concentrated solution of the neutral salt is boiled with hydrate of lime, and the mass washed with alcohol of 40° Bm., which dissolves the excess of neutral salt, without acting on the basic compound. Water decomposes it into hydrate of lime, and the normal salt which dissolves. (Millon, *J. Pharm.* 29, 184.)

*b. Mononitrate.—Lime Saltpetre; Wall Saltpetre.*—Found in several springs, and often in a state of efflorescence on walls, into which urine and other organic liquids penetrate. Formed also in nitre beds. Lime emits a feeble light when nitric acid is dropped upon it. (Heinrich.) The salt may be prepared by saturating aqueous nitric acid with lime or its carbonate, evaporating to dryness, and rendering the residue anhydrous by heat. White mass, having a sharp, warm, and bitter taste. May be heated to incipient fusion, without being decomposed. *Baldwin's Phosphorus* is prepared by melting the salt till the nitric acid begins to decompose. (I., 194.) When heated above its melting point, it evolves vapour of hyponitric acid and oxygen gas; detonates slightly with combustible substances.

| | Anhydrous. | | Wenzel. | Longchamp. | Richter. |
|---|---|---|---|---|---|
| CaO | 28 | 34·14 | 33·8 | 34·885 | 35·94 |
| $NO^5$ | 54 | 65·86 | 66·2 | 65·115 | 64·06 |
| $CaO, NO^5$ | 82 | 100·00 | 100·0 | 100·000 | 100·00 |

From an aqueous solution, the salt crystallizes in combination with 4 atoms of water. (Hess, Millon, *Compt. rend.* 14, 905.) Forms six-sided prisms with acute pyramidal summits. The crystals melt to an oily liquid when heated, and lose their water of crystallization at ordinary temperatures when placed over oil of vitriol in vacuo (Millon); they deliquesce rapidly in the air, dissolve in one-fourth their weight of water, and likewise very readily in alcohol. According to Mitscherlich (*Pogg.* 18, 159) the hydrated salt is precipitated as a crystalline powder from an aqueous solution by concentrated nitric acid.

| | Crystallized. | | Bergman. |
|---|---|---|---|
| CaO | 28 | 23·73 | 32 |
| $NO^5$ | 54 | 45·76 | 43 |
| 4HO | 36 | 30·51 | 25 |
| $CaO, NO^5 + 4Aq.$ | 118 | 100·00 | 100 |

C. Carbonate of Lime with Ammonia?—Lime-water and chloride of calcium are not at all, or but imperfectly precipitated in the cold, by aqueous ammonia which is but partially saturated with carbonic acid. Complete precipitation of carbonate of lime does not take place till the liquid has been heated, or has stood for a couple of days, or more carbonic acid gas is passed into it. (A. Vogel, *Ann. Chim.* 89, 128; *Schw.* 33, 204.)

D. Bromide of Calcium with Ammonia. — Bromide of calcium fused and then reduced to powder, absorbs ammoniacal gas with slight elevation of temperature, and is converted into a white voluminous powder. The compound forms with water a clear solution, which deposits

carbonate of lime on exposure to the air. (Rammelsberg, *Pogg. 55*, 239.)

| | Calculation. | | Rammelsberg. |
|---|---|---|---|
| $3NH^3$ | 51·0 | 34·14 | 34·4 |
| CaBr | 98·4 | 65·86 | 65·6 |
| $3NH^3$, CaBr | 149·4 | 100·00 | 100·0 |

E. Chloride of Calcium with Ammonia.—Chloride of calcium absorbs ammoniacal gas, swelling up and falling to powder. (Berzelius.) The fused chloride takes up the ammonia rapidly at first, but it is long before the absorption is complete; the lumps of chloride of calcium are thereby converted into a powder of 20 times their former volume. (H. Rose.) According to Persoz (*Ann. Chim. Phys.* 44, 317), recently fused chloride of calcium does not absorb ammonia. The compound loses all its ammonia at a moderate heat. (Faraday, H. Rose.) It takes fire in chlorine gas, with separation of nitrogen gas and formation of hydrochloric acid. (Faraday.) Water dissolves it perfectly, at the same time setting the ammonia free. (Faraday, H. Rose, *Pogg.* 20, 154.)

| | Saturated with Ammonia. | | H. Rose. |
|---|---|---|---|
| $4NH^3$ | 68·0 | 55·06 | 54·33 |
| CaCl | 55·5 | 44·94 | 45·67 |
| $4NH^3$, CaCl | 123·5 | 100·00 | 100·00 |

## Calcium and Potassium.

A. Phosphate of Lime and Potash.—When phosphate of potash is added to lime-water, or a concentrated aqueous solution of potash is boiled with phosphate of lime, an insoluble compound is produced, consisting of phosphoric acid, lime and potash, and a soluble compound of the same three elements, in which, however, the potash predominates. (Th. Saussure, *N. Gehl.* 2, 698; Berthollet, *N. Gehl.* 3, 274.)

B. Sulphate of Lime and Potash.—A mixture of the two salts fuses more readily than either of them alone. Water removes the sulphate of potash. (Braconnot, *Ann. Chim. Phys.* 31, 38.)

C. One atom of *Carbonate of Potash* fuses very easily with 1 or 2 atoms of *Fluor-spar*. The mass, when cool, is translucent, vitreous, and of a laminated crystalline texture; it deliquesces in the air, and water extracts from it carbonate of potash and fluoride of potassium; but the fluor-spar is never more than partially decomposed. The mixture when heated to whiteness, boils up and evolves carbonic acid, and then hardens. (Berthier, *Ann. Chim. Phys.* 38, 253.)

## Calcium and Sodium.

A. Carbonate of Lime and Soda.—*a. In atomic proportions.*—*α. Anhydrous.*—A mixture of 53·2 parts of dry carbonate of soda and 50 parts of carbonate of lime fuses very readily at a strong red heat, and forms a liquid as mobile as water; when rapidly cooled, it solidifies to a white transparent mass having a crystalline fracture. As soon as the heat rises above *bright redness*, the liquid boils and evolves carbonic acid,

then thickens, and at a white heat becomes perfectly solid. (Berthier, *Ann. Chim. Phys.* 38, 248.)

*β. Hydrated.*—Found native as *Gaylussite*, covering urao.—Precipitated occasionally, a little above 0°, from a solution of carbonate of soda purified by repeated crystallization; it is thus obtained in the form of a white powder, which is washed and dried. Gaylussite forms transparent, colourless, highly lustrous, oblique rhombic prisms belonging to the oblique prismatic system; $u : u^1 = 70\frac{1}{2}°$ &c.; cleavage parallel to $u$ and $u^1$. (Cordier.) The crystals refract light doubly. (G. Barruel.) Specific gravity from 1·928 to 1·95, *Boussingault.* (= 2·921, *Barruel.*) Harder than calc-spar.—Decrepitates slightly when heated: becomes opaque from loss of water, and fuses rapidly before the blowpipe to an opaque bead, which, when once formed, is no longer fusible, on account of the escape of carbonic acid (Berthier), and has a strong alkaline taste. Powdered Gaylussite before ignition dissolves sparingly in water without suffering decomposition; the anhydrous salt is resolved by water into carbonate of soda, which dissolves completely, and insoluble carbonate of lime. Nitric acid dissolves the mineral readily, with effervescence. (Boussingault, *Ann. Chim. Phys.* 31, 270; also *Schw.* 47, 247; also *Pogg.* 7, 97.) The artificially prepared salt effloresces in a dry atmosphere, and fuses on charcoal before the blowpipe to a clear bead, which solidifies on cooling to a white enamel; after long exposure to the flame, the carbonate of soda sinks into the charcoal, leaving the lime in a phosphorescent state. (Bauer, *Pogg.* 24, 367.)

| | Calculation. | | | | Boussingault. *Native.* | | Bauer. *Artif. Prep.* | |
|---|---|---|---|---|---|---|---|---|
| $NaO, CO^2$ ..... | 53·2 | .... | 35·89 | .... | 35·02 | .... | 36·2 | |
| $CaO, CO^2$ ..... | 50·0 | .... | 33·74 | .... | 32·49 | .... | 34·1 | |
| $5HO$ ..... | 45·0 | .... | 30·37 | .... | 32·49 | .... | 29·5 | |
| | 148·2 | .... | 100·00 | .... | 100·00 | .... | 99·8 | |

Barruel (*Ann. Chim. Phys.* 42, 313; also *Schw.* 58, 361) found in Gaylussite 14 per cent. of carbonate of soda, 70 of carbonate of lime, 9·7 of water, and 6 per cent. of impurities; probably he analysed a different mineral—a supposition which is corroborated by the high specific gravity which he found.

*b. One Atom of Carbonate of Soda and 2 Atoms of Carbonate of Lime* behave, when fused together, exactly like *a*. (Berthier.)

*c. One Atom of Carbonate of Soda and 3 Atoms of Carbonate of Lime.*—This mixture merely softens at a red heat, but afterwards boils and evolves carbonic acid. (Berthier.)

Carbonate of soda heated on charcoal before the blowpipe does not unite with caustic lime or carbonate of lime, but penetrates by itself into the pores of the charcoal. (Berzelius.)

B. Borax dissolves lime easily, forming with it a transparent glass; the carbonate of lime it dissolves with effervescence. The glass is transparent, but by exposure to an interrupted blast it becomes clouded; with a large excess of lime it solidifies, on cooling, to an angular crystalline mass. (Berzelius.)

¶ —Ulex (*Ann. Pharm.* 70, 49) describes a double borate of soda and lime occurring in the nitre-beds of Peru, and known by the name of *Tiza*, which is found in white masses from the size of a hazel-nut to that of a moderately sized potato. When broken, the mass is found to consist of

white, silky, crystalline threads interwoven with each other, which, according to Frankenheim, appear under the microscope to be six-sided prisms, or probably rhombic prisms with the more acute edges perpendicularly truncated in one direction, and obliquely in another. Sp. gr. = 1·8. Readily fuses before the blowpipe to a colourless glass. When moistened with sulphuric acid, it colours the flame green. Scarcely soluble in cold water, and very sparingly in hot; the solution has an alkaline reaction. Dissolves in acids without effervescence.

| | Calculation. | | | | Ulex. |
|---|---|---|---|---|---|
| NaO | 31·2 | .... | 8·99 | .... | 8·8 |
| 2CaO | 56·0 | .... | 16·13 | .... | 15·9 |
| $5BO^3$ | 170·0 | .... | 48·96 | .... | 49·5 |
| 10HO | 90·0 | .... | 25·92 | .... | 25·8 |
| NaO, 2CaO, $5BO^3$ + 10Aq. | 347·2 | .... | 100·00 | .... | 100·0 |

This substance appears to be similar, if not identical, with Hayes's *Hydro-borocalcite*, or, according to the above, *Boro-natrocalcite.* ¶

C. *Metaphosphate of Soda* (as it remains after fusion of phosphate of soda and ammonia) dissolves *lime* abundantly before the blowpipe—the carbonate also with effervescence. The bead, which is transparent while hot, does not become milky on cooling unless it is saturated with lime. (Berzelius.)

One part of *Bone-ash* forms, at a red heat, with 3·8 parts of dry *Carbonate of Soda*, a fluid mixture, which, when solidified, resembles close-grained, white statuary marble, and at a white heat evolves carbonic acid and becomes less fusible. With 1·9 parts of carbonate of soda, at a red heat, it forms a soft pasty mass; but with less carbonate of soda it does not fuse at all. (Berthier.)

D. Sulphide of Calcium and Sodium.—By exposing 10 parts of dry sulphate of soda with 25 parts of crystallized gypsum to a white heat in a charcoal crucible, part of the sulphide of sodium formed is volatilized; and 14·15 parts of a metallic sulphide are obtained, consisting of 26 per cent. of sulphide of sodium and 74 of sulphide of calcium (probably a mere mixture of the two). Rose-coloured, blistered mass having a granular fracture and somewhat pearly lustre. At a stronger white heat it loses still more sulphide of sodium, and leaves a dense granular mass. (Berthier, *Ann. Chim. Phys.* 22, 245.)

E. Sulphate of Soda with Carbonate of Lime.—One atom of sulphate of soda with one atom of carbonate of lime, or one atom of carbonate of soda with one atom of sulphate of lime, fuses tranquilly at a red heat, without evolving gas, and yields on cooling, a clear, white, solid mass, having a somewhat crystalline, granular fracture. Heated to whiteness, it parts with carbonic acid, and is converted into an infusible mixture of caustic lime and sulphate of soda. (Berthier.)

F. Sulphate of Lime and Soda.—Found in the form of *Glauberite.*—Transparent, colourless, oblique rhombic prisms. Fig. 100 (nearly); $u : u^1 = 80° 8'$; $i$ : the edge between $u$ and $u^1 = 111° 13'$; cleavage parallel to $u$ and $u^1$, and most distinct, parallel to $i$. Sp. gr. from 2·73 to 2·8. Fuses before the blowpipe to a clear bead, which becomes turbid as it cools. Becomes opaque when put into water. (Brogniart, J. Min. 23, 5.)

By fusing the sulphates of soda and lime together, in atomic proportions a pellucid mass is obtained resembling chalcedony. (Berthier.)

G. *Common Salt and Carbonate of Lime*, when fused together in atomi proportions, yield a white transparent mass having an uneven fracture and becoming infusible when heated to whiteness. (Berthier.)

H. 100·8 parts (1 At.) of anhydrous *borax* form with 116·1 part of *Fluor-spar* at a white heat, a not very fluid mixture, which solidifie to a dense mass, with scaly fracture. (Berthier, *Ann. Chim. Phys.* 4 296.)

I. One atom of *Sulphate of Soda* and one atom of *Fluor-spar* fu together at a white heat, forming a thin liquid, which on cooling yields dense translucent mass, of crystalline granular fracture. With 2 atoms fluor-spar the mixture does not fuse quite so well, but yields a simila though harder mass on cooling. (Berthier.)

K. One atom of common salt and one atom of fluor-spar heated to inc pient whiteness, fuse together to a thin liquid, and emit a white clou The mass, when cool, is compact and translucent, and has a crystallin foliated fracture. (Berthier.)

## Calcium and Barium.

A. Compound of Lime and Baryta.—Equal parts of lime and ba ryta heated together unite and form a greenish glass, which, however contains silica derived from the crucible. (Guyton-Morveau.)

B. Carbonate of Lime and Baryta.—Found native as *Barytocal cite*.—Sometimes (*a*) oblique rhombic prisms; $u : u = 106° 54'$; $i : u = 102° 54'$; specific gravity = 3·646 (Brooke, *Ann. Phil.* 24, 114); some times (*b*) right rhombic prisms, analogous to that of Arragonite; specific gravity = 3·7; it is consequently dimorphous. (Johnston, *Phil. Mag. J.* 6, 1; 10, 373.)

| | Calculation. | | Children. |
|---|---|---|---|
| $BaO, CO^2$ | 98·6 | 66·35 | 65·9 |
| $CaO, CO^2$ | 50·0 | 33·65 | 33·6 |
| $BaO, CO^2 + CaO, CO^2$ | 148·6 | 100·00 | 99·5 |

This mineral contains from 2·3 to 6·6 per cent. of carbonate of strontia. (Johnston.)

C. Sulphate of Lime and Baryta.—Found native as *Dreelite*. Small truncated rhombohedrons; (*Fig.* 141) $r^3 : r^5 = 93°$ to 94°; cleavage plane parallel to the *r*-surfaces. Specific gravity = 3·3; somewhat harder than calc-spar. Formula: $2(BaO, SO^3) + CaO, SO^3$. (Dufrenoy, *Ann. Chim. Phys.* 60, 102; also *J. pr. Chem.* 7, 165.)

D. One atom of *Sulphide of Barium* with one atom of *Fluor-spar* forms at a white heat a soft pasty mass, which when cool becomes brown, opaque, and dense, and exhibits a granular fracture. The same substance *is obtained* when heavy-spar and fluor-spar are heated together in a char*coal crucible*. (Berthier.)

E. One atom of *Heavy-spar* fuses but imperfectly with one atom of *Fluor-spar*, and yields a blistered mass having a crystalline granular fracture. With 2 atoms of heavy spar the mixture becomes perfectly fusible, and yields a dense transparent mass, of slightly crystalline fracture. (Berthier.) Sulphate of baryta heated with fluor-spar before the blowpipe on charcoal forms a glass which is clear while fused, but enamel-white when cold. (Berzelius.)

F. One atom of *Chloride of Barium* fuses pretty readily with 1 or 2 atoms of *Fluor-spar*, emitting acid vapours. The product is an opaque enamel, exhibiting a splintered fracture. Water removes chloride of barium from it, and leaves fluor-spar; but alcohol dissolves out from the powdered enamel a considerable quantity of chloride of calcium; fluoride of barium must therefore have been formed. (Berthier.)

## Calcium and Strontium.

A. Lime and Strontia.—Equal parts of these substances fuse to a hard, white, blistered cake, which contains a few glassy and enamel-like globules. (Guyton-Morveau.)

B. Carbonate of Lime and Strontia.—*Emmonite* contains 82·7 per cent. of carbonate of strontia with 12·5 per cent. of carbonate of lime. (Thomson, *J. pr. Chem.* 13, 234.)

C. *Sulphate of Strontia* fuses with *Fluor-spar* on charcoal before the blowpipe to a clear glass, which becomes enamel-white on cooling. (Berzelius.)

## Calcium and Calcium.

A. *Carbonate of Lime and Chloride of Calcium* in atomic proportions fuse together very easily at a red heat; when exposed to a white heat, the mixture loses carbonic acid and solidifies. (Berthier, *Ann. Chim. Phys.* 38, 253.)

¶ B. Sulphide of Calcium and Lime.—$CaS, + CaO, HO$. According to H. Rose, this compound cannot be prepared on the small scale, but is produced in the preparation of carbonate of soda from the sulphate, &c., and remains undissolved on treating the mass with water. (*Ann. Pharm.* 50, 439.) ¶

C. Sulphide of Calcium with Chloride of Calcium.—One atom of sulphate of lime heated to whiteness in a charcoal crucible with one atom of chloride of calcium, forms a semi-fluid paste, which on cooling becomes black and translucent, and exhibits a highly crystalline fracture; it deliquesces rapidly in the air. (Berthier, *Ann. Chim. Phys.* 43, 303.)

D. Triphosphate of Lime with Chloride or Fluoride of Calcium.—Apatite is sometimes found as *Chlorapatite* $= 3(3CaO, PO^5) + CaCl$; sometimes as *Fluorapatite* $= 3(3CaO, PO^5) + CaF$, but most frequently as *a mixture of the two*. (H. Rose, *Pogg.* 9, 185.) It belongs to

ıe rhombohedral system of crystallization (*Fig.* 135, 137, 138, 139, 140 nd others); $p : r = 157° 47' 32''$. (Hauy.) Specific gravity = 3·225. Mohs.)

| | Chlorapatite. | | | Fluorapatite. | | H. Rose. |
|---|---|---|---|---|---|---|
| 9CaO..... | 252·0 | 48·31 | 9CaO ..... | 252·0 | 49·91 | 92·31 |
| $3cPO^5$ .... | 214·2 | 41·07 | $3cPO^5$ .... | 214·2 | 42·42 | |
| CaCl..... | 55·4 | 10·62 | CaF ..... | 38·7 | 7·66 | 7·69 |
| | 521·6 | 100·00 | | 504·9 | 99·99 | 100·00 |

E. Sulphide of Calcium with Fluoride of Calcium.—One atom of sulphate of lime fuses readily with one atom of fluor-spar, and yields a white, scarcely translucent, blistered mass, exhibiting a crystalline granular fracture. (Berthier.)

F. Sulphate of Lime with Fluoride of Calcium.—*a.* One atom of sulphate of lime with 2 atoms of fluor-spar: Fuses perfectly, forming a dense mass with uneven and slightly crystalline fracture.—*b.* In atomic proportions: Fuses with still greater ease. Clear white mass, formed of large plates crossing each other, with spaces filled with crystals.—*c.* 2 atoms of sulphate of lime with one atom of fluor-spar: Fuses completely but less readily than *b*. White, semi-transparent, compact masses, with shining, granular-foliated fracture.—*d.* 4 atoms of sulphate of lime with one atom of fluor-spar: Fuses but very imperfectly. White, opaque, highly blistered mass, with fine-grained fracture. (Berthier.)

Before the blowpipe, 7 parts of gypsum yield with 4 parts of fluor-spar a mass which is transparent while fused, but becomes enamel-white on cooling; after prolonged ignition, it loses sulphuric acid and becomes infusible,—the change being attended with some degree of effervescence and the formation of cauliflower-like excrescences. (Berzelius.)

Calcium also combines with mercury.

CHAPTER VII.

# MAGNESIUM.

Bergman de Magnesia. *Opusc.* 1, 365.
Fourcroy. *Ann. Chim.* 2, 278.
Berzelius. *Gilb.* 40, 255.—Further: *Schw.* 31, 258; also *Ann. Chim. Phys.* 14, 370.

*Magnium. Talcium.*

*History.* The knowledge of carbonate of magnesia, or *magnesia alba*, as a medicine was first promulgated from Rome in the beginning of the 18th century; Valentin in 1707 and Slevogt in 1709 subsequently found the same earth in the mother-liquor of saltpetre and in Epsom salts; Hoffmann, Black, Marggraf, and Bergman pointed out the characters which distinguish it from lime, with which it was at first confounded; Sir H. Davy obtained from it the metal magnesium, which Bussy succeeded in procuring in a greater degree of purity.

*Sources.* Less abundant than calcium; found in the inorganic kingdom as hydrate, carbonate, borate, phosphate, sulphate, hydrochlorate, and nitrate of magnesia, sometimes in the solid state, sometimes dissolved in various mineral waters (including salt springs), and in sea-water; in a variety of minerals, consisting of silicate of magnesia combined with other silicates, as in soap-stone, meerchaum, steatite, ophite, tolite, anorthite, hornblende, asbestos, talk, augite, chrysolite, and—combined with alumina—in spinell and zeilanite; in the organic kingdom, chiefly as carbonate and phosphate, and in combination with organic acids.

*Preparation.*—1. Into the closed end of a glass tube, about half an inch wide and 20 inches long, bent down at a short distance from the bottom, 6 globules of potassium about the size of peas are introduced, and into the horizontal portion, pieces of chloride of magnesium separated from each other by small fragments of porcelain or glass, to prevent their running together. This portion of the tube is then heated nearly to redness; after which the potassium is made to boil. The vapour of the potassium, acting on the chloride of magnesium, gives rise to vivid ignition, which gradually spreads throughout the tube. When cold, the chloride of potassium and undecomposed chloride of magnesium are dissolved out from the mass by means of cold water deprived of air by boiling, and the globules of magnesium are washed two or three times with water. On first adding the water, a small quantity of hydrogen gas is evolved, arising from the presence of free potassium, and the potash thus produced preci-

pitates a small portion of hydrate of magnesia from the chloride of
nesium; this however is easily removed by washing. (Bussy, *J. Chim.*
6, 141; also *Schw.* 59, 218; also *Pogg.*18, 140.)—Liebig (*Pogg.* 19,
introduces into a straight glass tube from 3 to 4 lines in diameter
closed at one end, about 10 or 20 globules of potassium of the size of
and above them, chloride of magnesium in large pieces; heats the v
over a charcoal fire; and then inclines the tube so as to suffer the
potassium to permeate the chloride of magnesium: decomposition
takes place with incandescence. The small globules obtained after wa
the cooled mass, are made to unite into one large globule, by heating
with chloride of potassium in a closed crucible to the melting point o
ver.—2. Vapour of potassium is passed over magnesia ignited in a plat
tube, and the residue gently heated with mercury, which dissolve
magnesium and may be afterwards separated by distillation. (H. Dav
3. By the first method given for the preparation of barium. Slightly
tened magnesia is not decomposed with the same readiness as slightly
tened sulphate of magnesia; the mercury also cannot be completely
tilled from the amalgam obtained, since magnesium when heated acts
glass. (H. Davy.) Gay-Lussac & Thénard did not succeed in prod
the amalgam by the galvanic method.—4. If the glass tube *a* and the
*c* (App. 8) are filled with a saturated solution of common salt, an
glass tube *b* with a saturated solution of chloride of magnesium, the
tive electrode of a battery consisting of 20 pairs of plates being ma
pass into *a* and the negative electrode into *b*, no metal is deposited o
cathode from the magnesium salt, unless it has been prepared in a
vessel and has taken up a small quantity of chloride of silver. In
case, it first deposits, with a scarcely perceptible evolution of hyd
gas, a grey mixture of silver and magnesium, and afterwards pure
nesium in silver-white octohedrons. (Becquerel.)

*Properties.* Silver-white, with a high lustre; very ductile and ca
of being beaten out into thin leaves; fuses at a gentle heat. (Bu
Hard, yielding however to the hammer and the file. (Liebig.) Cry
lizes in octohedrons. (Becquerel.)

*Atomic weight of Magnesium:* 12·11 (Scheerer, *Pogg.* 70, 407);
(Svanberg & Nordenfeldt, *J. pr. Chem.* 45, 473).

## *Compounds of Magnesium.*

### Magnesium and Oxygen.

### Magnesia. MgO.

*Oxide of Magnesium, Magnesia, Calcined Magnesia, Talkerde, Bitte
Magnesie, Oxyde de Magnesium, Magnesia usta* v. *calcinata.*

*Formation.* The metal remains permanent in dry air; in moist
becomes slowly but only superficially covered with a white cru
magnesia; heated in very small pieces in the air, it burns with li
emission of sparks, and forms magnesia; larger portions are difficult to
completely. (Bussy.) It inflames at the temperature at which b
glass softens, emitting a most vivid light. Magnesia is deposited on
sides of the vessel in which the combustion takes place, and the pa
*the tube on* which the metal lay exhibits a black spot which cannc

removed by boiling with acids; this effect is probably due to the separation of silicium. (Liebig.) Cold water previously freed from air by boiling has no effect on magnesium; boiling water however evolves a few bubbles of hydrogen gas; acidulated water dissolves the metal easily, with disengagement of hydrogen gas; oil of vitriol in which it is digested evolves sulphurous acid; and cold nitric acid gives off binoxide of nitrogen. (Liebig.)

*Preparation.* By gentle but prolonged ignition of carbonate of magnesia.

*Impurities.*—1. *Carbonate of Magnesia:* Occurs when the magnesia has not been ignited for a sufficient length of time, or from long exposure to the air, even after thorough ignition. The moistened earth effervesces with hydrochloric acid.—2. *Lime:* The hydrochloric acid solution neutralized with ammonia is rendered turbid by oxalate of ammonia.—3. *Oxides of the heavy metals,* as *Oxide of Manganese:* The hydrochloric acid solution supersaturated with sulphuretted hydrogen water gives a characteristic precipitate with ammonia.—4. *Silica:* Remains undissolved after digestion in hydrochloric acid.—5. *Sulphate* or *Hydrochlorate of Potash* or *Soda:* Arising from the carbonate of magnesia not having been sufficiently washed. Water boiled with the earth and filtered gives the reactions of sulphuric or hydrochloric acid, and leaves a saline residue after evaporation.

*Properties.* Fine, white, very voluminous powder; specific gravity = 3·200 (Karsten); = 3·07 (Richter); = 2·3 (Kirwan); = 3·61 after ignition in the porcelain furnace. (H. Rose.) Fuses only at the very highest temperatures, as in a fire fed with oxygen gas—its surface then acquires the appearance of porcelain-glaze. (Guyton-Morveau.) It also fuses, though with great difficulty, in the oxy-hydrogen blowpipe flame, to which it communicates a pale red colour, and is then converted into a sort of opaque glass or enamel which scratches glass like the diamond (Clarke, *Ann. Phil.* 17, 421); also under the influence of a very powerful voltaic current (H. Davy). Tasteless and inodorous. Changes some of the more delicate vegetable colours, *e. g.* moistened red litmus paper, in the same manner as the alkalis. It is not caustic. Moistened with nitrate of cobalt and strongly ignited before the blowpipe, it takes a fine rose-colour. (Berzelius.)

| | Calculation. | | Henry, Wollaston. | Gay-Lussac. | Berzelius. | Hisinger. | Sir H. Davy. |
|---|---|---|---|---|---|---|---|
| Mg..... | 12 | 60 | 59·3 | 59·5 | 61·29 | 61·7 | 66 |
| O ..... | 8 | 40 | 40·7 | 40·5 | 38·71 | 38·3 | 34 |
| MgO .... | 20 | 100 | 100·0 | 100·0 | 100·00 | 100·0 | 100 |

(MgO = 158·35 + 100 = 258·35. Berzelius.)

*Decompositions.*—1. By potassium at a white heat.—2. By voltaic electricity. (H. Davy.)—When magnesia mixed up with oil is exposed to the oxy-hydrogen flame, a slag is obtained, which crumbles in the air to a white powder consisting of magnesia. (Clarke.)

*Combinations.*—*a.* With water.—*α.* Hydrate of Magnesia.—Found native. Ignited magnesia evolves heat when mixed with water. (H. Davy.) On the addition of either cold or hot water, the magnesia instantly becomes saturated with it. (Rees.) 1. Magnesia is moistened with water, and then dried in a water-bath. (Rees.) 2. To the aqueous

solution of a salt of magnesia, potash or soda is added in excess, and the precipitate well washed. The natural variety has a laminated structure and belongs to the rhombohedral system of crystallization. (*Fig.* 135.) Its specific gravity is 2·336 (Brewster); it is soft, white, transparent, and of a pearly lustre; the artificially prepared hydrate is a white powder or, when dried at 100°, a semitransparent, coherent, soft, very brittle mass. It gives up its water below a red heat.

| | Calculation. | | Berzelius. *Artif.* | | Sir H. Davy. *Artif.* | Stromeyer. *Native.* |
|---|---|---|---|---|---|---|
| MgO | 20 | 69 | 69·4 to 70·2 | | 75 | 68·35 |
| HO | 9 | 31 | 30·6 ,, 29·8 | | 25 | 30·90 |
| Protoxides of Iron and Manganese | | | | | | 0·75 |
| MgO, HO | 29 | 100 | 100·0 | 100·0 | 100 | 100·00 |

| | Fyfe. *Native.* | Bruce, Nuttal. *Native.* | Rees. *Artif.* |
|---|---|---|---|
| MgO | 69·75 | 70 | 69·52 |
| HO | 30·25 | 30 | 30·48 |
| | 100·00 | 100 | 100·00 |

*β.* Solution of Magnesia.—Magnesia dissolves in 5142 parts of water at 15·5° (60° F.) (Fyfe), in 5800 parts of water at 15° (O. Henry, *J. Pharm.* 13, 2), in 7900 (Kirwan), in 16,000 parts (Dalton) of cold water, and in 36,000 parts of boiling water. (Fyfe, *Edinb. Phil. J.* 5, 305.) ¶ In 55,368 parts of water, either boiling or at ordinary temperatures. The solution has a feeble alkaline action, and gives, after some time a scanty precipitate with phosphate of soda, on the addition of ammonia. (Fresenius, *Ann. Pharm.* 59, 117.) ¶ The presence of lime, sulphate of lime or sulphate of potash in water does not interfere with its solvent powers on magnesia. (O. Henry.)

*b.* With acids, producing the Magnesia-Salts, Magnesia has less affinity for acids than the six fixed alkalis; nevertheless it neutralizes them perfectly. The salts of magnesia are colourless, when the acid with which it is combined is destitute of colour; they have a bitterish taste when soluble in water. The acid if volatile is expelled by ignition, with the exception of sulphuric acid. The magnesia-salts, moistened with nitrate of cobalt and strongly heated in the blowpipe flame, become rose-coloured. (Berzelius.) Phosphate of magnesia, however, takes a violet tint. (Wittstein.) All the salts of magnesia which are insoluble in water, *e.g.*, the carbonate, borate, phosphate, and arseniate—the ignited metaphosphate, however, excepted—dissolve in hydrochloric acid. Those magnesia salts which are soluble in water, are completely decomposed by potash and soda, even in the cold, depositing the hydrate of magnesia in copious flakes. The precipitate disappears on the addition of sulphate, nitrate, hydrochlorate, or succinate of ammonia, and likewise with the carbonate, though the latter deposits crystals after a while. (Wittstein.) A small addition of ammonia does not affect the neutral magnesia-salts; a larger quantity precipitates hydrate of magnesia (in combination with a very small portion of acid: *Berzelius*); but even a large excess of ammonia never separates more than half the magnesia present (Fourcroy, *Crell. Ann.* 1792, 1, 451): for the ammoniacal salt produced unites with *the still undecomposed* salt of magnesia, and forms a double salt, which is

not further decomposed either by ammonia or by magnesia. (*Vid.* I., 132, and *Sch.* 95.) Hence ammonia, even in excess, gives little or no precipitate with a salt of magnesia, when mixed with a considerable quantity of sal-ammoniac or of free acid; and the turbidity produced by ammonia in the solution of a salt of magnesia disappears again completely on the addition of sal-ammoniac. An aqueous solution of sulphate of magnesia, containing one part of magnesia in 4000 parts of water, gives a cloud with ammonia after a few seconds. (Harting.) Sesqui-carbonate of ammonia precipitates magnesia within twenty-four hours, and the more rapidly and completely in proportion to the strength of the solution and the quantity of sesqui-carbonate employed. It is to be remarked that the precipitate obtained by a small addition of carbonate of ammonia is carbonate of magnesia, whilst that produced by an excess consists of double carbonate of magnesia and ammonia. (Guibourt, *J. Chim. Med.* 1, 418.) One part of sesqui-carbonate of ammonia added to 2 parts of sulphate of magnesia, precipitates one half of the base as carbonate; but 2 parts of sesqui-carbonate of ammonia added to one part of the same salt, precipitates the whole of the magnesia in the form of double carbonate of magnesia and ammonia. This precipitate is soluble in water, but not in an aqueous solution of carbonate of ammonia; it therefore redissolves, after a few days, in the supernatant liquid, in consequence of that liquid losing its carbonate of ammonia by exposure to the air. (Guibourt.) According to Pfaff, sesqui-carbonate of ammonia precipitates the greater part of the magnesia, though not the whole; according to Longchamp, a small portion only, after two days; according to J. Dulong (*J. Pharm.* 11, 406), it causes precipitation much more slowly when dilute than when concentrated. Carbonate of potash or soda separates from neutral magnesia-salts, in the cold, only a small quantity of a basic carbonate of magnesia, which is again dissolved either by an excess of the magnesia salt or of the alkaline carbonate (H. Rose, *Pogg.* 34, 157), the rest of the magnesia remaining dissolved as an acid salt. With the aid of heat, nearly all the magnesia is thrown down; but in this case also, according to Longchamp (*Ann. Chim. Phys.* 12, 255; also *Gilb.* 66, 24), the precipitation is less complete, in proportion to the quantity of carbonate, sulphate, hydrochlorate, or nitrate of potash or soda contained in the liquid: the precipitate likewise diminishes as the liquid cools. It is easily dissolved by sal-ammoniac, and, therefore, when the magnesia salt is mixed with sal-ammoniac, no precipitate is produced, except on boiling. Sesqui-carbonate of soda does not affect a tolerably dilute solution of a magnesia-salt in the cold (Schindler, *Mag. Pharm.* 33, 29); with a solution of sulphate of magnesia, it does not give a precipitate, till after the lapse of two days. (Boussingault.) Bicarbonate of ammonia, potash, or soda, produces a precipitate only on boiling. In the cold, the bicarbonate of magnesia produced, remains dissolved by the alkaline salt; but on boiling the solution, it loses carbonic acid. Borax precipitates the magnesia salts with the aid of heat, but not in the cold. Ordinary diphosphate of soda gives no precipitate in the cold, except with the most concentrated solutions. With more dilute solutions the aid of heat is required, but the precipitate then formed does not disappear on cooling. When caustic ammonia or carbonate of ammonia is added to a dilute solution of any salt of magnesia mixed with phosphate of soda, or when phosphate of ammonia or of soda is added to the mixture of a magnesia-salt with sal-ammoniac and ammonia, the magnesia is very completely precipitated in the form of *phosphate of* magnesia and ammonia, which, according to

Wollaston, attaches itself in a crystalline granular condition to the sides of the glass vessel, especially where they have been touched by the glass rod in stirring. A solution containing only $\frac{1}{200000}$ parts of magnesia gives a precipitate after 24 hours, with phosphate of ammonia mixed with free ammonia, provided the latter solution is highly concentrated and added in equal quantity; if, however, it is dilute and added in smaller quantity, it does not give any indication of magnesia in a solution containing $\frac{1}{1000}$ part of that substance. (Harting, *J. pr. Chem.* 22, 50.) Mono-tungstate of soda causes a precipitate only in very concentrated solutions of magnesia salts; when more dilute they continue clear, even after the addition of ammonia. (Anthon.) Oxalic acid and binoxalate of potash precipitate even dilute solutions of magnesia salts, on the addition of ammonia, provided no free acid or sal-ammoniac is present, and the oxalic acid, or the acid oxalate of potash is not added in too large an excess. In the contrary case, the ammoniacal salt, whether already present, or formed on adding the ammonia, retains the oxalate of magnesia in solution. (H. Rose.) Ferrocyanide of potassium produces, after some time, a dense white precipitate. (H. Rose.) Magnesia-salts are not precipitated by sulphuric acid or the sulphates, or by perchloric acid, hydrofluosilicic acid, bi-hydrosulphate of ammonia, carbonate of lime (Fuchs), or ferricyanide of potassium. Magnesia forms double salts with ammonia, potash, soda, lime, &c.

*c.* With several earths, producing minerals and fused masses.—*d.* With certain substances in the organic kingdom.

## Magnesium and Carbon.

Carbonate of Magnesia.—Magnesia absorbs carbonic acid very slowly from the air.—*a. Two-thirds Carbonate.*—Sulphate of magnesia is precipitated by a very large excess of carbonate of soda, and the whole boiled till the precipitate is observed by the microscope to be passing from the floculent to the granular condition; it is then washed and boiled rapidly with water, the liquid poured off, and the residue twice boiled with fresh quantities of water.—Small grains, mixed with a small quantity of the original floculent precipitate. (Fritzsche, *Pogg.* 37, 310.) The precipitate may contain carbonate of soda. (Berzelius, *Jahresber.* 17, 158.)

| | Calculation. | | Fritzsche. |
|---|---|---|---|
| 3MgO | 60 | 45·80 | 47·23 |
| $2CO^2$ | 44 | 33·59 | 32·67 |
| 3HO | 27 | 20·61 | 20·10 |
| $3MgO, 2CO^2 + 3Aq.$ | 131 | 100·00 | 100·00 |

It may also be regarded as $MgO, HO + 2(MgO, CO^2 + 2Aq.)$

*b. Three-fourths Carbonate.*—Found in the mineral kingdom as *Hydromagnesite.*—1. Sulphate of magnesia is mixed hot with an excess of carbonate of potash, and the precipitate boiled with fresh quantities of water, as long as an acid carbonate of magnesia continues to be dissolved. (Berzelius.)—2. From a saturated solution of carbonate of magnesia in aqueous carbonic acid, the carbonate of magnesia is thrown down by boiling, and the precipitate twice reboiled with fresh quantities of water. (Fritzsche.) The native variety resembles chalk; the artificially prepared salt is a white powder. It is soluble, according to Fyfe, in 2493 parts of cold, and in 9000 parts of boiling water. The solution has an alkaline

reaction. (Pleischl.) It is dissolved in the cold by an aqueous solution of carbonate of potash or soda, and also by a solution of sulphate, hydrochlorate, or nitrate of potash, and probably by other salts. On heating the solution, it separates in part only, and is again dissolved as the liquid cools. (Longchamp.) It is easily soluble in sulphate, hydrochlorate, nitrate, or succinate of ammonia; and likewise in the carbonate; but this solution deposits crystals after a while. (Wittstein.)

| | Calculation. | | Berzelius. *Artif.* | | Trolle-Wachtmeister. *Nat.* | | Kobell. *Nat.* | |
|---|---|---|---|---|---|---|---|---|
| 4MgO | 80 | 43·96 | 44·58 | | 42·41 | | 43·96 | |
| $3CO^2$ | 66 | 36·26 | 35·70 | | 36·82 | | 36·00 | |
| 4HO | 36 | 19·78 | 19·72 | | 18·53 | | 19·68 | |
| Silica, oxide of iron, &c. | | | | | 2·24 | | 0·36 | |
| $4MgO,3CO^2 + 4Aq.$ | 182 | 100·00 | 100·00 | | 100·00 | | 100·00 | |

It may also be regarded as $MgO,HO + 3(MgO,CO^2 + Aq.)$

*c. Four-fifths Carbonate.*—1. Formed by boiling the crystals of penta-hydrated monocarbonate of magnesia with pure water. In order to obtain the compound quite free from ter-hydrated monocarbonate of magnesia, it is best to boil the crystals for a considerable time with water containing ammonia, the ammonia being frequently renewed during the process.—2. A concentrated solution of carbonate of magnesia in aqueous carbonic acid is boiled for a long time.—White granular powder. The grains when examined by the microscope, appear to be composed of a fibrous mass arranged in concentric layers. (Fritzsche.)

| | Calculation. | | Fritzsche. | Berzelius, according to 2. | |
|---|---|---|---|---|---|
| 5MgO | 100 | 42·92 | 42·10 | 42·8 | 43·2 |
| $4CO^2$ | 88 | 37·76 | 36·22 | 36·5 | 36·4 |
| 5HO | 45 | 19·32 | 21·68 | 20·7 | 20·4 |
| $5MgO,4CO^2 + 5Aq.$ | 233 | 100·00 | 100·00 | 100·0 | 100·0 |

It may be regarded as $MgO,HO + 4(MgO,CO^2 + Aq.)$

### *Magnesia Alba.*

This substance is prepared on the large scale by precipitating the sulphate, hydrochlorate, or nitrate of magnesia with carbonate of potash or soda. For this purpose, a solution of sulphate of magnesia is used; also various mineral waters (*Bitterwasser*) and the mother-liquor of sea-water, many salt springs, and many kinds of nitre; most of these liquids, however, likewise contain lime, which must previously be separated by sulphate of potash or soda. According to Durand (*Ann. Chim. Phys.* 54, 312; also *Ann. Pharm.* 10, 140), a solution of 100 parts of sulphate of magnesia in 100 parts of water is rapidly mixed in a wooden tub or barrel heated by steam with a solution of 125 parts of deca-hydrated carbonate of soda. The temperature is raised to 80° (172° F.) to expel carbonic acid, which would otherwise retain a portion of magnesia in solution; and the clear liquid is decanted from the precipitate. This is washed three times, by subsidence and decantation, with lukewarm water free from lime, then thrown on large linen filters, and allowed to drain from 24 to 48 hours. The wet mass is then conveyed into square boxes without bottoms, standing on a surface of gypsum or of brick,

through which the water rapidly soaks; the boxes are turned over after some time, in order that the upper portion may be dehydrated also; and the blocks of carbonate of magnesia thus obtained are thoroughly dried in heated chambers.

Magnesia alba, according to Berzelius, is hydrated $\frac{3}{4}$-carbonate of magnesia, containing a certain portion of hydrated monocarbonate, the quantity of which increases in proportion as the liquid is less boiled after the precipitation. According to Fritzsche, it consists wholly or for the most part of $\frac{4}{5}$-carbonate of magnesia. The constitution of magnesia alba is affected by the following circumstances: 1. *The relative quantity of the precipitant.* When an excess of carbonate of soda is used, the precipitate retains a portion of that reagent, and is thereby rendered more dense; when sulphate or hydrochlorate of magnesia is in excess, it contains a small quantity of sulphuric or hydrochloric acid, and is lighter; carbonate of potash may be used in excess. (Berzelius.) The precipitate does not become granular with an excess of the alkaline carbonate so readily as with an excess of the magnesia salt. (Fritzsche.) [In Durand's method the carbonate of soda somewhat predominates.]—2. *Degree of dilution.* The more dilute the two solutions are, the lighter is the precipitate, and the more normal salt does it contain. (Berzelius.) [Durand, on the contrary, employs concentrated solutions.]—3. *Temperature.* The precipitate formed in the cold consists chiefly of hydrated normal salt; a large quantity of magnesia at the same time remaining in solution, because the normal salt is resolved by the action of the water into an insoluble basic salt, and an acid salt which is dissolved. On applying heat, the carbonic acid is expelled from this solution, and the greater part of the magnesia is thrown down; at the same time, the remaining normal salt contained in the original precipitate is resolved into a basic salt, and carbonic acid which escapes. When this mixture is boiled for a long time, the precipitate is converted into $\frac{3}{4}$-carbonate of magnesia. The salt is lightest when precipitated in the cold. (Berzelius.) When moderately boiled, which is usually the case, the precipitate is converted into the $\frac{4}{5}$-carbonate; but by continuing the operation, it becomes mixed with a constantly increasing quantity of the $\frac{3}{4}$ and $\frac{2}{3}$-carbonates of magnesia. (Fritzsche.) The utmost degree of lightness is obtained by allowing the precipitate to freeze while still moist. (Berzelius.) Magnesia alba stirred up with water manifests a slight alkaline reaction. (Pleischl.) It dissolves readily in water containing sal-ammoniac; with greater difficulty, however, after being heated to 100°. The saturated solution has a weak alkaline reaction; does not become turbid by exposure to the air, or by boiling; is precipitated by potash; and when treated with acids, evolves abundance of carbonic acid gas. (A. Vogel, *J. pr. Chem.* 7, 455.)

Commercial magnesia alba.

| | Kirwan. | Bergman. | Butini. | Dalton. *Dried at* 100°. | Klaproth. | Fourcroy. |
|---|---|---|---|---|---|---|
| MgO ..... | 45 .... | 45 .... | 43 .... | 43 .... | 40 .... | 40 |
| $CO^2$ ..... | 34 .... | 25 .... | 36 .... | 40 .... | 33 .... | 48 |
| HO..... | 21 .... | 30 .... | 21 .... | 17 .... | 27 .... | 12 |
| | 100 .... | 100 .... | 100 .... | 100 .... | 100 .... | 100 |

Prepared on the small scale. $c$ = precipitated cold; $h$ = precipitated hot; M = with an excess of magnesia salt; *Alk.* = with an excess of carbonate of potash.

| | Bucholz. | | Berzelius. | | |
|---|---|---|---|---|---|
| | *h.* | *c.* | *h., M.* | *h., Alk.* | *c., M.* |
| MgO | 42 | 33 | 42·24 | 43·16 | 36·40 |
| $CO^2$ | 35 | 32 | 37·00 | 36·47 | 30·25 |
| HO | 23 | 35 | 20·76 | 20·37 | 33·35 |
| | 100 | 100 | 100·00 | 100·00 | 100·00 |

[See also Deane and Gladstone, *Pharmaceutical Journal*, vol. VIII. No. 6.]

*d. Monocarbonate.*—Found in the mineral kingdom as *Magnesite.*—Magnesite belongs to the rhombohedral system of crystallization; forms obtuse rhombohedrons. (*Fig.* 141) $r^3 : r^5 = 107° 25'$; $r^1 : r^3$ or $r^5 = 72° 35'$. Specific gravity = 3·056 (Mohs). It may be obtained as a crystalline powder, exhibiting the form of arragonite when examined by the microscope, by evaporating to dryness with the aid of heat, a solution of carbonate of magnesia in aqueous carbonic acid. (H. Rose, *Pogg.* 42, 366.) Powdered magnesite, when moistened with water, gives an alkaline reaction with litmus and violets. (Pleischl. *Zeitschr. Phys. v. W.* 5, 59.)

| | *Magnesite.* | | Klaproth. | Stromeyer. |
|---|---|---|---|---|
| MgO | 20 | 47·62 | 48 | 47·64 |
| $CO^2$ | 22 | 52·38 | 49 | 50·75 |
| Water and other impurities | | | 3 | 1·61 |
| MgO, $CO^2$ | 42 | 100·00 | 100 | 100·00 |

*α. Ter-hydrated Monocarbonate of Magnesia.*—1. A solution of carbonate of magnesia in aqueous carbonic acid is allowed to evaporate spontaneously in the air (Berzelius), or kept for a long while at a temperature of 50°. (Fritzsche.)—2. The tabular crystals of the penta-hydrated salt are exposed in a glass tube to the sun's rays, whereby they lose 2 atoms of water.—3. The latter salt is heated for a long time in water at 50°, or boiled with water till it becomes opaque and begins to evolve carbonic acid; it is then left to itself in the cold, and in the course of a day or two is converted into a net-work of crystals of the ter-hydrated salt. The water also with which the tabular crystals are heated till carbonic acid begins to escape, but not to the boiling point—yields, on cooling, crystals of the salt, a portion of which it had previously dissolved. (Fritzsche.)—4. A mixture of the aqueous solutions of sulphate of magnesia and bicarbonate of potash or soda is set aside till crystals appear. (Fourcroy; V. Rose.) The precipitate which the normal carbonate of soda gives with sulphate of magnesia is likewise converted in a few days, at temperatures between 0° and + 10°, into crystals of the terhydrated salt. (Fritzsche, Soubeiran, *J. Pharm.* 13, 596.) A mixture of sulphate of magnesia and sesquicarbonate of soda, which is perfectly clear at first, also yields this salt after the lapse of two days, in the form of a crystalline deposit at the bottom of the vessel. (Boussingault, *Ann. Chim. Phys.* 29, 285.) Forms small needles collected together in tufts; permanent in the air (Fritzsche); effloresces in a dry atmosphere (Berzelius); hard, with a slightly alkaline taste; turns the juice of violets green. (Soubeiran.) The salt when gently ignited loses its acid together with its water. Cold water dissolves but a very small quantity (according to Fourcroy, one part in 48 parts of water); the solution evolves carbonic acid on boiling, and deposits magnesia alba. (Soubeiran.) The solution in cold water is accompanied by the formation of an acid salt, whilst a $\frac{3}{4}$-carbonate of magnesia

remains undissolved; boiling water takes up nothing, but expels carbonic acid, giving rise to the formation of a $\frac{3}{4}$-carbonate. (Berzelius.) Boiling water does not produce any decomposition. (Fritzsche, *Pogg.* 37, 304.)

| | Crystallized salt. | | Soubeiran. | | Berzelius. | | Buch., W. Henry, Boussingault. |
|---|---|---|---|---|---|---|---|
| MgO | 20 | 28·99 | 29·58 | | 29·6 | | 30 |
| $CO^2$ | 22 | 31·88 | 31·50 | | 31·5 | | 30 |
| 3HO | 27 | 39·13 | 38·92 | | 38·9 | | 40 |
| MgO, $CO^2$ + 3Aq. | 69 | 100·00 | 100·00 | | 100·0 | | 100 |

*β. Penta-hydrated Monocarbonate.*—A saturated solution of carbonate of magnesia in aqueous carbonic acid, exposed to the cold of winter in loosely covered vessels, deposits crystals of the ter-hydrated and of the penta-hydrated salt; the quantity of the latter increasing in proportion to the degree of cold. Transparent tabular crystals. (Fritzsche.) The crystals belong to the oblique prismatic system. (*Fig.* 116) $i : u$ or $u^1 = 102°$; $i : \alpha = 120° 30'$; $u : u^1 = 86° 30'$; $u : t = 133° 15'$; $u : m = 136° 45'$. (Brooke, *Ann. Phil.* 22, 275.) The crystals, on exposure to the air, part very slowly with 2 atoms of water, and become opaque; more rapidly, however, in the direct rays of the sun; in hot water even at 50° they lose their transparency, being converted into salt *d*, *α*, with evolution of carbonic acid. If the crystals are boiled as long as this action continues, they become converted, without change of form, into a white incoherent mass of $\frac{4}{5}$-carbonate, which is also frequently mixed with crystals of the *d*, *α* salt. (Fritzsche.)

| | Crystallized salt. | | Fritzsche. |
|---|---|---|---|
| MgO | 20 | 22·99 | 23·70 |
| $CO^2$ | 22 | 25·29 | 25·39 |
| 5HO | 45 | 51·72 | 50·91 |
| MgO, $CO^2$ + 5Aq. | 87 | 100·00 | 100·00 |

*ε. Bicarbonate.*—Magnesia alba shaken up with aqueous carbonic acid yields a solution having a bitter taste and an alkaline reaction. (Berthollet, *N. Gehl.* 3, 263.) Even with a large excess of carbonic acid, and also after boiling, the solution exerts an alkaline reaction on logwood, turmeric, and rhubarb (Pfaff, *Schw.* 35, 428); it also turns reddened litmus blue (Pleischl, Gmelin); according to Berthollet, it gives a green colour with violets, but red with litmus. The saturated solution contains exactly twice as much carbonic acid as the normal salt. (Soubeiran.) It becomes turbid at 75°, but recovers its transparency again on cooling. (Berthollet.) When heated even to 50°, it deposits ter-hydrated monocarbonate (Berzelius, Fritzsche); the same thing occurs when it is evaporated in vacuo, half the carbonic acid escaping. (Soubeiran, *J. Pharm.* 13, 598.)

## Magnesium and Boron.

### Borate of Magnesia.

*a. Triborate.*—1. Formed by boiling a solution of sulphate of magnesia with solution of borax, and washing the precipitate thoroughly with cold water.—2. By boiling a solution of borate of magnesia and soda *in cold water.* (Wöhler.) The boiling is continued for a long time, and *the liquid* filtered hot; but the precipitate remaining on the filter is

washed with cold water, because hot water would withdraw a portion of the acid; it is then dried under a bell-jar over oil of vitriol. (Rammelsberg, *Pogg.* 49, 445.) The freshly precipitated salt is gelatinous, but after drying it becomes white and gritty. (Wöhler.) It is slightly soluble in cold water; the solution has an alkaline reaction, is rendered turbid by boiling, and when evaporated leaves a transparent varnish. By long continued boiling with a large quantity of water, or by washing with boiling water, part at least of the boracic acid is separated from the salt, and the residue dries up to a white mass, which is insoluble in cold water, and absorbs carbonic acid from the air. (Wöhler, *Pogg.* 28, 525.)

| | Ignited. | Rammelsberg. | | | Hydrated. | Rammelsberg. |
|---|---|---|---|---|---|---|
| 3MgO ..... | 60·0 | 63·29 | 61·84 | 3MgO.... | 60·0 | 34·13 | 32·42 |
| $BO^3$ ..... | 34·8 | 36·71 | 38·16 | $BO^3$ .... | 34·8 | 19·80 | 20·62 |
| | | | | 9HO .... | 81·0 | 46·07 | 46·96 |
| $3MgO,BO^3$.... | 94·8 | 100·00 | 100·00 | + 9Aq. | 175·8 | 100·00 | 100·00 |

*b. Monoborate?* An aqueous solution of sulphate of magnesia and borax (heated till it becomes turbid, and again rendered clear by cooling) set aside for some months, and kept during part of the time at temperatures below 0°, yields long, slender, transparent needles collected together in tufts. They become milk-white when heated, and fall to pieces when wholly deprived of their water of crystallization. They are not soluble either in cold or in hot water, but readily soluble in hydrochloric acid. From a solution in warm concentrated hydrochloric acid, boracic acid crystallizes out on cooling; from a more dilute solution, ammonia precipitates the salt in fine needles. The crystals contain 16·67 per cent. of magnesia, 25·00 of boracic acid, and 58·33 of water. (Wöhler.)

*c. Four-thirds Borate.*—Found in nature as *Boracite.* Transparent and colourless cubes with dodecahedral and tetrahedral surfaces (*Fig.* 17). Specific gravity = 2·955. (Rammelsberg.) Harder than felspar. Heated in the blowpipe flame on charcoal, it fuses with difficulty, and forms a clear yellowish bead, which on cooling solidifies to a crystalline enamel-like mass, covered with needles. (Berzelius.) Insoluble in water but slowly dissolved by acids.

| | *Boracite.* | | Arfvedson. | Rammels-berg. | Stro-meyer. | Pfaff. |
|---|---|---|---|---|---|---|
| 3MgO ..... | 60·0 | 30·12 | 30·3 | 30·75 | 33 | 36·3 |
| $4BO^3$..... | 139·2 | 69·88 | 69·7 | 69·25 | 67 | 63·7 |
| $3MgO,4BO^3$ .... | 199·2 | 100·00 | 100·0 | 100·00 | 100 | 100·0 |

It may be regarded as 2 ($MgO,BO^3$) + $MgO,2BO^3$. (Berzelius.)

*d. Terborate.*—Hydrate of magnesia or magnesia alba in excess is boiled with boracic acid in water, filtered, and evaporated to the crystallizing point. Granular crystals. (Wöhler.) Crystalline crust. (Rammelsberg.) Has an alkaline reaction, and, when ignited, loses water, together with part of its boracic acid, leaving a fused spongy mass. The salt yields pure boracic acid to boiling water, and a residue is left which appears to be hydrate of magnesia. It dissolves in cold water slowly, but in tolerable quantity; the solution does not become turbid on boiling, and is precipitated by ammonia, only when concentrated. (Wöhler, *Pogg.* 28, 527.) It is soluble in 75 parts of cold water. (Rammelsberg.)

| | Crystallized. | | Rammelsberg. |
|---|---|---|---|
| MgO | 20·0 | 10·18 | 10·79 |
| $3BO^3$ | 104·4 | 53·16 | 53·54 |
| 8HO | 72·0 | 36·66 | 35·67 |
| $MgO, 3BO^3 + 8Aq.$ | 196·4 | 100·00 | 100·00 |

*c. Sexborate.* Sometimes produced in the form of a granular powder together with *d*, in the preparation of *d* with magnesia alba. When ignited, it bakes together and forms a mass resembling porcelain. (Rammelsberg, *Pogg.* 49, 455.) Sexborate of potash does not precipitate the salts of magnesia. (Laurent.)

| | Calculation. | | Rammelsberg. |
|---|---|---|---|
| MgO | 20·0 | 5·12 | 5·585 |
| $6BO^3$ | 208·8 | 53·43 | 54·184 |
| 18HO | 162·0 | 41·45 | 40·231 |
| $MgO, 6BO^3 + 18Aq.$ | 390·8 | 100·00 | 100·000 |

## Magnesium and Phosphorus.

A. Hypophosphite of Magnesia.—Hypophosphite of lime is boiled for a considerable time with oxalate of magnesia and water, and the filtrate evaporated.—Large regular octohedrons, possessing considerable hardness. They effloresce in dry air; and, when ignited, yield a considerable quantity of water, together with spontaneously inflammable phosphuretted hydrogen gas, and leave a residue of a reddish colour. The crystals digested with nitric acid, and then evaporated to dryness, leave 69·11 per cent. of monophosphate of magnesia. (H. Rose, *Pogg.* 12, 85.)

| | Crystallized. | | H. Rose. |
|---|---|---|---|
| MgO | 20·0 | 15·22 | 15·48 |
| PO | 39·4 | 29·99 | 29·60 |
| 8HO | 72·0 | 54·79 | 54·92 |
| MgO, 2HO, PO + 6Aq. | 131·4 | 100·00 | 100·00 |

B. Phosphite of Magnesia.—Sulphate of magnesia does not give a precipitate with phosphite of ammonia. The salt is formed by boiling magnesia alba with very dilute phosphorous acid, and leaving the filtrate to evaporate in vacuo over oil of vitriol. Forms a crystalline crust. Ignited in a retort, it yields a large quantity of water, and likewise hydrogen gas, the first portions of which are tolerably pure, but the latter are mixed with phosphorus. The salt becomes incandescent as it changes into phosphate, and yields 47·9 per cent. of phosphate of magnesia, tinged with red from the presence of phosphoric oxide. Water dissolves it with difficulty. (H. Rose, *Pogg.* 9, 28.)

C. Ordinary Phosphate of Magnesia.—*a. Triphosphate.* Present in small quantities in vegetables, as in the seeds of the cereal grasses, and also in animal bodies, as in the bones, in urinary calculi, and in bezoar-stones. Formed artificially by precipitating sulphate of magnesia with triphosphate of soda. The precipitate dried at 100° still retains 5 atoms of water. When the salt *b* is boiled with water, this compound separates in combination with 5 atoms of water. (Rammelsberg.) The salt is

readily soluble in acids, even after exposure to a white heat (by which it is converted into a transparent glass.) (Graham.)

| | After ignition. | | | | Dried at 100° C. | | |
|---|---|---|---|---|---|---|---|
| 3MgO | 60·0 | .... | 45·66 | 3MgO | 60·0 | .... | 34·01 |
| $cPO^5$ | 71·4 | .... | 54·34 | $cPO^5$ | 71·4 | .... | 40·48 |
| | | | | 5HO | 45·0 | .... | 25·51 |
| 3MgO, $cPO^5$ | 131·4 | .... | 100·00 | + 5Aq. | 176·4 | .... | 100·00 |

*b. Diphosphate.*—1. A solution of 2 parts of sulphate of magnesia in 32 parts of water, mixed with a solution of 3 parts of ordinary diphosphate of soda in 32 parts of water, deposits the salt in the course of 24 hours in the form of needles. (Fourcroy, Riffault, Graham.)—2. A solution of magnesia in phosphoric acid (Bergman), or a mixture of acetate of magnesia with phosphoric acid (Berzelius), evaporated slowly, also yields crystals of this salt.—Small six-sided prisms and needles, having a slightly cooling and sweetish taste. (Fourcroy.) The crystals effloresce rapidly in the air. At 100°, they lose 8 atoms of water; at 176° (348·8° F.), 6 atoms more; and at a stronger heat, the 15th atom, which was present in a basic capacity. The residue, after strong ignition [di-pyrophosphate of magnesia?], is insoluble in acids. (Graham.) If the heat is further increased, a transparent glass is produced. (Fourcroy.) After several days' digestion with cold water, 1 part of the crystallized salt dissolves in 322 parts of the water; the solution becomes turbid at 49°, and milky at 100°, in consequence of a portion of the salt separating unchanged, although in a very bulky and amorphous state. The boiling hot solution contains only 1 part of the salt in 498 parts of water; but on cooling, a part of that which has been precipitated is slowly redissolved. (Graham.) According to Riffault (*Ann. Chim. Phys.* 19, 90), boiling water, decomposes the diphosphate into a soluble acid salt, and a basic salt which remains undissolved. ¶ Schaffer (*Ann. Pharm.* 50, 145) finds, that the basic residue left after treating the diphosphate with boiling water, as long as the filtrate remains acid, consists of $3MgO, PO^5, 2HO + 5$ Aq., as observed by Rammelsberg (*vid. supra*); the acid solution evaporated in vacuo over oil of vitriol yielded a very acid mass, resolved by strong alcohol into a basic salt and free phosphoric acid, which dissolved a portion of the undecomposed salt. ¶ The salt is much more soluble in water containing a trace of phosphoric, sulphuric, hydrochloric, nitric, oxalic, or acetic acid; and a solution thus obtained does not become turbid on boiling. (Graham, *Phil. Mag. Ann.* 2, 20; also *Ann. Pharm.* 29, 24.)

Without water of crystallization.

| | | | |
|---|---|---|---|
| 2MgO | 40·0 | .... | 33·21 |
| $cPO^5$ | 71·4 | .... | 59·30 |
| HO | 9·0 | .... | 7·49 |
| 2MgO, HO, $cPO^5$ | 120·4 | .... | 100·00 |

| Crystallized, according to Graham. | | | | | Riffault. |
|---|---|---|---|---|---|
| 2MgO | 40·0 | .... | 16·23 | .... | 46·98 |
| $cPO^5$ | 71·4 | .... | 28·98 | | |
| HO | 9·0 | .... | 3·65 | .... | 53·02 |
| 14Aq. | 126·0 | .... | 51·14 | | |
| + 14Aq. | 246·4 | .... | 100·00 | .... | 100·00 |

¶ D. Di-pyrophosphate of Magnesia.—Remains in the form of a transparent glass after the fusion of phosphate of magnesia and ammonia. Di-pyrophosphate of soda gives no precipitate with sulphate of magnesia till after the addition of carbonate of ammonia; it then throws down di-pyrophosphate of magnesia containing but a trace of ammonia, and soluble with tolerable facility in an excess of carbonate of ammonia, and likewise in pyrophosphate of soda. (Wach. *Schw.* 59, 207.) The precipitate resembles hydrate of alumina in appearance. When dissolved in aqueous solution of sulphurous acid and boiled, it is obtained in the form of a crystalline powder. (Schwarzenberg.)

| | Calculation. | | | | Schwarzenberg. Amorphous. | | Crystallized. | |
|---|---|---|---|---|---|---|---|---|
| 2MgO ..... | 40·0 | .... | 35·9 | .... | 35·61 | .... | 35·8 | |
| $PO^5$ ..... | 71·4 | .... | 64·1 | .... | 63·57 | .... | 63·9 | |
| 2MgO, $PO^5$ .... | 111·4 | .... | 100·0 | .... | 99·18 | .... | 99·7 | |

The crystals contain 3 atoms of water. (Schwarzenberg, *Ann. Pharm.* 65, 2.) ¶

E. Metaphosphate of Magnesia. 1. Metaphosphate of soda gives with the acetate, but not with the sulphate of magnesia, a soft tenacious precipitate. (Graham.)—¶ 2. The salt is also formed by dissolving carbonate of magnesia in excess of dilute phosphoric acid, evaporating the solution to dryness, and heating the residue to a temperature of 316°. (Maddrell, *Mem. Chem. Soc.* 3, 273, 1848.)

| | Calculation. | | | | Maddrell. | |
|---|---|---|---|---|---|---|
| MgO ..... | 20·0 | .... | 22·453 | .... | 22·470 | |
| $PO^5$ ..... | 71·4 | .... | 77·547 | .... | 77·424 | |
| MgO, $PO^5$.... | 91·4 | .... | 100·000 | .... | 99·894 | ¶ |

## Magnesium and Sulphur.

A. Sulphide of Magnesium.—Magnesium cannot be made to combine with sulphur by fusion. (Liebig.)—100 parts of anhydrous sulphate of magnesia exposed to a white heat in a charcoal crucible, leave 39·5 parts of a white friable residue, which in 100 parts contains 78·0 parts of magnesia, 7·2 parts of magnesium, and 12·0 parts of sulphur; it may be regarded as a mixture of magnesia and sulphide of magnesium. Boiling water dissolves out [bi-]hydrosulphate of magnesia and leaves the magnesia behind. A mixture of sulphate of magnesia and charcoal yields very little sulphide of magnesium after ignition, the product consisting almost wholly of magnesia. (Berthier, *Ann. Chim. Phys.* 22, 236.)

*Hydrated Sulphide of Magnesium*, or *Monohydrosulphate of Magnesia.*—Separates on evaporating an aqueous solution of the bi-hydrosulphate of magnesia in vacuo, or on mixing that salt with a concentrated solution of bi-hydrosulphate of potash, inasmuch as the latter withdraws the water from the magnesia salt;—or on mixing concentrated solutions of chloride of magnesium and bi-hydrosulphate of potash: in either case sulphuretted hydrogen gas is set free.—Greyish viscid mass, dissolving in acids with evolution of sulphuretted hydrogen. (Berzelius.)

B. Hydrated double Sulphide of Hydrogen and Magnesium, or Bi-hydrosulphate of Magnesia.—1. Hydrate of magnesia diffused in water through which a stream of sulphuretted hydrogen gas is passed, is slowly but abundantly dissolved, and this compound is produced.—2. A similar solution, but containing an alkaline salt, is produced by mixing a salt of magnesia with the bi-hydrosulphate of an alkali in a dilute state. When too small a quantity of water is present, the compound cannot exist, but is resolved into mono-hydrosulphate of magnesia, which is precipitated, and sulphuretted hydrogen, which escapes.—The solution prepared according to the first method is resolved by evaporation in vacuo or in an atmosphere of hydrogen gas—also on being mixed with concentrated bi-hydrosulphate of potash—into sulphuretted hydrogen gas and insoluble mono-hydrosulphate of magnesia. By boiling, it loses all its sulphuretted hydrogen and deposits hydrate of magnesia. (Berzelius, *Pogg.* 6, 442.)

C. Hyposulphite of Magnesia.—Prepared by boiling a solution of sulphite of magnesia with flowers of sulphur. (Herschel.) The filtrate evaporated over oil of vitriol yields small, transparent, colourless, rectangular prisms, with rhombo-octohedral summits and with the terminal edges replaced by planes. They are permanent in the air, but lose about half their water of crystallization at 170°. They fuse and are decomposed by a strong heat, evolving water, sulphur, and sulphurous acid, and leaving after ignition, 30·75 per cent. of a white semifused mass, consisting of sulphite, sulphate, and pure magnesia.—Easily soluble in water; from a concentrated aqueous solution it is precipitated by alcohol in the form of an oily liquid. (Rammelsberg, *Pogg.* 56, 303.)

| | Crystallized. | | | | Rammelsberg. |
|---|---|---|---|---|---|
| MgO | 20·0 | .... | 16·40 | .... | 16·82 |
| $S^2O^2$ | 48·0 | .... | 39·34 | .... | 39·23 |
| 6HO | 54·0 | .... | 44·26 | .... | 43·95 |
| $MgO,S^2O^2 + 6Aq.$ | 122·0 | .... | 100·00 | .... | 100·00 |

D. Sulphite of Magnesia.—A white powder, which crystallizes in tetrahedrons (oblique rhombic prisms: *Muspratt*), when its solution in aqueous sulphurous acid is evaporated; tastes earthy at first, and sulphurous afterwards.—It contains 16 per cent. of magnesia, 39 of sulphurous acid, and 45 of water (according to Muspratt, 33·85 per cent. of water =3 atoms).—Softens when heated, and loses first water and then acid. When exposed to the air, it is gradually converted into sulphate, becoming opaque at the same time.—Sulphite of magnesia is soluble in 20 parts of cold and in a somewhat smaller quantity of hot water. (Fourcroy & Vauquelin.)

E. Hyposulphate of Magnesia.—Formed by precipitating the hyposulphate of baryta with sulphate of magnesia.—Ill-defined, six-sided prisms; very bitter; permanent in the air. When heated, they fuse in their own water of crystallization, and leave, after ignition, 40·775 per cent. of sulphate of magnesia. The salt is soluble in 0·85 parts of water at 3°. The solution may be boiled without undergoing decomposition. (Heeren.)

| | Crystallized. | | Heeren. |
|---|---|---|---|
| MgO | 20 | 13·70 | 13·87 |
| $S^2O^5$ | 72 | 49·31 | 48·44 |
| 6HO | 54 | 36·99 | 37·69 |
| MgO, $S^2O^5$ + 6Aq | 146 | 100·00 | 100·00 |

F. Sulphate of Magnesia.—*a.* Monosulphate. *Bittersalt; Seidschütz Salt, Seidlitz Salt; Epsom Salts; Sal amarum, anglicum, cathartícum.*—Found in the crystalline state; also in magnesia-springs, in certain salt-springs, and in sea-water; effloresces on many walls and rocks. (*Vid.* Stromeyer & Hansmann, *Schw.* 69, 256.)—When magnesia is mixed with fuming oil of vitriol, combination takes place accompanied by incandescence.

*Preparation.*—1. By evaporating magnesia waters.—2. From the mother-liquor of sea-water and of many salt-springs; also from that obtained in the manufacture of alum. The chloride of magnesium obtained in the first process is distilled with sulphuric acid, and thus converted into sulphate, hydrochloric acid being obtained as a by-product. (Liebig, *Ann. Pharm.* 35, 111.)—3. By dissolving native carbonate of magnesia in dilute sulphuric acid. For this purpose, either the pure carbonate of magnesia known as magnesite may be used, (*vid.* Anthon, *J. pr. Chem.* 9, 1,) or the double carbonate of magnesia and lime, which occurs in the form of dolomite, &c. The latter is first ignited, slaked with water, and then treated with half the quantity of pyroligneous or of hydrochloric acid necessary to dissolve the whole. In this manner the lime is separated by elective affinity, and the washed residue, consisting of magnesia, is treated with sulphuric acid or solution of green vitriol. (Henry, *Ann. Chim. Phys.* 6, 86.)—4. Serpentine containing magnetic pyrites, is washed and exhausted with water. The serpentine of Mount Ramasso at Genoa, which contains veins of magnetic pyrites and copper pyrites, is roasted in alternate layers with wood in pits or furnaces. It is then exposed for some months to the air and frequently moistened with water; after which, the sulphate of magnesia, which exudes in a state of efflorescence, is dissolved out by water—the copper separated from the filtrate by means of iron—and the iron by a quantity of burnt dolomite, just sufficient for the precipitation. The liquid is then filtered, and evaporated to the crystallizing point. (Mojon, Holland, *Ann. Chim. Phys.* 4, 249.)—*Purification.* By prolonged and gentle ignition, solution in water, boiling with calcined magnesia, filtration, and crystallization.

*Impurities.*—1. *Sulphate of Soda:* The solution precipitated with baryta-water, and the filtrate freed from excess of baryta by carbonate of ammonia, and then evaporated to dryness and ignited, leaves carbonate of soda. Or: A cold solution shaken up with carbonate of baryta becomes strongly alkaline. (Kölreuter.) Or: The anhydrous salt ignited with half its weight of charcoal yields sulphide of sodium when digested in water. (Pagenstecher.)—2. *Chloride of Magnesium:* A tendency to absorb moisture from the air; precipitate with a very dilute solution of nitrate of silver.—3. *Sulphate of Manganese:* A solution mixed with sal-ammoniac and ammonia, in a close vessel containing air, deposits, after a while, brown hydrated sesqui-oxide of manganese; the same effect is produced on passing chlorine through a solution to which bicarbonate of potash has been added.—4. *Sulphate of the protoxide* or *sesqui-oxide of iron.* Precipitate with sulphide of ammonium, and other

characters of iron.—5. *Sulphate of Copper.* Brown precipitate or colour with sulphuretted hydrogen.

On igniting the crystals, a white opaque mass is obtained, of specific gravity 2·6066 (Karsten); it has a bitter taste, and, according to Pleischl, turns reddened litmus blue. The salt sustains a moderate red heat without decomposition. By exposure for eight hours to a strong red heat, it loses one-fourth of its acid and becomes partially insoluble in water: after ignition for a still longer time, it appears to be no longer soluble in water, but only in hydrochloric acid, emitting an odour of sulphuretted hydrogen. (Daubeny, *Edinb. Phil. J.* 7, 111.) [This odour would lead to the supposition that the loss of sulphuric acid was due to the action of some reducing agent from the fire, and not to the heat alone.]—By heating dry sulphate of magnesia to redness with charcoal, a mixture of one volume of carbonic acid gas and two volumes of sulphurous acid gas is obtained, together with free sulphur, the residue consisting of magnesia free from sulphide of magnesium. (Gay-Lussac, *J. pr. Chem.* 11, 68.) At a white heat, a small quantity of sulphide of magnesium is formed at the same time. (Berthier, III., 234.)—Ammonia in excess throws down from an aqueous solution of this salt a translucent, granular precipitate which rapidly collects at the bottom; it contains 67·5 per cent. of the earth, 1·6 of sulphuric acid, and 30·9 of water. (Berzelius.)—Sulphate of magnesia is not decomposed by aqueous hydrochloric acid, and crystallizes without alteration from a solution in this acid, on evaporation and cooling. (Kane.)—An aqueous solution is decomposed by double affinity, when mixed with chloride of ammonium, chloride of potassium, or nitrate of potash; the alkaline sulphate produced unites with undecomposed sulphate of magnesia to form a double salt. (Karsten.) The affinities brought into play between sulphate of magnesia and common salt vary with the temperature. (I., 131.)—A recently prepared mixture of crystallized sulphate of magnesia and bicarbonate of soda dissolves in water without turbidity; but a similar mixture, after being kept for some months, deposits carbonate of magnesia. (Planche, *J. Pharm.* 12, 131.)

| | After ignition. | | | | Henry. | | Gay-Lussac. |
|---|---|---|---|---|---|---|---|
| MgO ..... | 20 | .... | 33·33 | .... | 32·14 | .... | 33 to 33·1 |
| $SO^3$ ..... | 40 | .... | 66·67 | .... | 67·86 | .... | 67 „ 66·9 |
| MgO, $SO^3$ .... | 60 | .... | 100·00 | .... | 100·00 | .... | 100 to 100·0 |

| | Berzelius. | | | Wenzel. | | Kirwan. |
|---|---|---|---|---|---|---|
| | *Earlier.* | | *Later.* | | | |
| MgO ..... | 33·36 | .... | 34 | .... 35·5 | .... | 36·68 |
| $SO^3$ ..... | 66·64 | .... | 66 | .... 64·5 | .... | 63·32 |
| | 100·00 | .... | 100 | .... 100·0 | .... | 100·00 |

*Combinations with Water.* Sulphate of magnesia, after ignition, evolves considerable heat on being mixed with water. (Richter.) Exposed to the air, it slowly absorbs water. 100 parts of the ignited salt absorbed from the air in ten days during the month of June, 103·05 parts of water (7 At.), but no more afterwards. (Blücher.)

α. *With one atom of water.*—Prepared by heating crystallized sulphate of magnesia to 132° (269·6° F.) in the air. This last atom of water is

not expelled below 210°—238° (410—460·4° F). Graham distinguishes it from the water of crystallization by the name of *constitutional* water.

*β. With two atoms of water.* Obtained by drying the crystallized salt in vacuo over oil of vitriol at 100°. At a temperature of 22° (71·6° F.) in vacuo or 100° in the air, rather more than 2 atoms of water are left behind. (Graham, *Phil. Mag. Ann.* 6, 422.)

*γ. With six atoms of Water.* Crystallizes from a solution evaporated by heat till a crystalline film forms on the surface, and then set aside for some time in a warm place. Opaque crystals, similar in form to those of borax, but with different angles. (Haidinger, *Pogg.* 6, 191.) When the crystals of the 7-hydrated salt are gradually heated, they suddenly, at 52°, give off one atom of water, and are converted into an aggregate of small prisms of the salt γ, converging from without towards the centre of the mass. (Mitscherlich.) Hence it appears that the dimorphism described (I., 132), according to Mitscherlich's earlier statement, does not really exist, the quantity of water being different in the two cases.

| | Calculation. | | |
|---|---|---|---|
| MgO ..... | 20 | .... | 17·54 |
| $SO^3$ ..... | 40 | .... | 35·09 |
| 6HO ..... | 54 | .... | 47·37 |
| MgO, $SO^3$ + 6Aq. .... | 114 | .... | 100·00 |

*δ. With 7 atoms of Water.*—The ordinary form of sulphate of magnesia.—Crystallizes from a warm and not too concentrated solution by cooling or by spontaneous evaporation. Transparent prisms and needles, belonging to the right prismatic system. (*Fig.* 71 & 72) $u^1 : u = 90°\ 30'$; $u^1 : t = 134°\ 45'$; $u^1 : a^1 = 129°$; $y$ above : $y$ below = 120° (nearly) cleavage parallel to $t$. (Brooke, *Ann. Phil.* 22, 40.) Specific gravity = 1·751 (Mohs), = 1·674. (Kopp.) Effloresces only in warm dry air, and then but slightly; when gently heated, it fuses and becomes anhydrous.

| | Crystallized. | | Long-champ. | Gay-Lussac. | Wen-zel. | Kirwan. | Mitscher-lich. |
|---|---|---|---|---|---|---|---|
| MgO..... | 20 | 16·26 | 13·25 | 16·04 | 16·86 | 17·00 | 48·8 |
| $SO^3$ ..... | 40 | 32·52 | 33·75 | 32·53 | 30·64 | 29·35 | |
| 7HO..... | 63 | 51·22 | 53·00 | 51·43 | 52·50 | 53·65 | 51·2 |
| MgO, $SO^3$ + 7Aq. | 123 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·0 |

| | Henry. | A. Vogel. *Native.* | Mojon. | Bergman. | Dalton. | Berzelius. |
|---|---|---|---|---|---|---|
| MgO ..... | 48·473 | 18 | 19 | 19 | 19 | 19·07 |
| $SO^3$ ..... | | 33 | 32 | 33 | 37 | 38·15 |
| 7HO ..... | 51·527 | 48 | 49 | 48 | 44 | 42·78 |
| | 100·000 | 99 | 100 | 100 | 100 | 100·00 |

Several of these last analyses were probably made with the sex-hydrated salt.

*ε. With 12 atoms of Water.*—A saturated solution of sulphate of magnesia is resolved, below 0°, into a mass of ice and crystals, which are obtained separate after the slow thawing of the ice at 0°. Prepared in small quantities they are opaque, but when made on the large scale, transparent. Above 0° they give off water, and are converted into opaque

seven-hydrated salt, without, however, changing their form. (Fritzsche, *Pogg.* 42, 577.)

| | Calculation. | | Fritzsche. |
|---|---|---|---|
| $MgO, SO^3$ ..... | 60 .... | 35·71 .... | 36·13 |
| 12HO ..... | 108 .... | 64·29 .... | 63·87 |
| $MgO, SO^3 + 12Aq.$ | 168 .... | 100·00 .... | 100·00 |

Sulphate of magnesia, after ignition, dissolves very slowly in water, previously crumbling to a fine powder; the crystals dissolve very rapidly. 100 parts of water at 0° dissolve 25·76 parts of the anhydrous salt, and 0·47816 parts for every degree beyond. (Gay-Lussac.) One part of the seven-hydrated salt dissolves in 0·799 parts of water at 18·75° (65.75° F.), forming a liquid of specific gravity 1·2932. A saturated solution at 8° (46·4° F.), has a specific gravity of 1·267. (Anthon.) Sulphate of magnesia dissolves much more rapidly and abundantly in aqueous hydrochloric acid than in water, yielding a clear syrupy liquid. (Richter, *Stöchiom.* 2, 245.)

*Strength of an Aqueous Solution of Sulphate of Magnesia, at* 15° (59° F.) *according to Anthon (J. pr. Chem. 9, 3).*

| Sp. gr. | Per cent. | Sp. gr. | Per cent. | Sp. gr. | Per cent. | Sp. gr. | Per cent. |
|---|---|---|---|---|---|---|---|
| 1·270 | 47·36 | 1·150 | 28·57 | 1·107 | 20·63 | 1·055 | 10·71 |
| 1·250 | 44·44 | 1·147 | 28·05 | 1·104 | 20·00 | 1·050 | 9·91 |
| 1·230 | 41·17 | 1·145 | 27·53 | 1·101 | 19·35 | 1·046 | 9·09 |
| 1·207 | 37·50 | 1·143 | 27·01 | 1·098 | 18·69 | 1·043 | 8·25 |
| 1·174 | 33·33 | 1·140 | 26·47 | 1·095 | 18·03 | 1·039 | 7·41 |
| 1·172 | 32·88 | 1·137 | 25·92 | 1·091 | 17·35 | 1·034 | 6·54 |
| 1·170 | 32·43 | 1·134 | 25·37 | 1·088 | 16·66 | 1·029 | 5·66 |
| 1·168 | 31·97 | 1·131 | 24·81 | 1·084 | 15·96 | 1·024 | 4·76 |
| 1·166 | 31·51 | 1·128 | 24·24 | 1·080 | 15·25 | 1·020 | 3·84 |
| 1·164 | 31·03 | 1·124 | 23·66 | 1·075 | 14·52 | 1·016 | 2·91 |
| 1·161 | 30·55 | 1·120 | 23·07 | 1·072 | 13·79 | 1·010 | 1·96 |
| 1·158 | 30·06 | 1·117 | 22·48 | 1·068 | 13·04 | 1·006 | 0·99 |
| 1·155 | 29·57 | 1·114 | 21·87 | 1·064 | 12·28 | | |
| 1·153 | 29·07 | 1·111 | 21·26 | 1·059 | 11·50 | | |

G. Sulphide of Carbon and Magnesium and Hydrosulphocarbonate of Magnesia.—Hydrosulphocarbonate of baryta is precipitated by sulphate of magnesia and the filtrate evaporated in vacuo; a film forms on its surface, and a portion of bisulphide of carbon evaporates. The dry salt is of a pale lemon colour, and not crystalline. Cold water dissolves it but partially, acquiring a deep yellow tint and a hot peppery taste. The insoluble residue is a *basic salt*, which is decomposed by boiling water, imparting to it a yellow colour, and leaving a residue of carbonate of magnesia. (Berzelius.)

## Magnesium and Selenium.

A. Selenide of Magnesium?—An aqueous solution of selenide of potassium gives with salts of magnesia a flesh-coloured precipitate from which acids separate selenium; it likewise evolves selenium when ignited. (Berzelius.)

B. Bi-hydroseleniate of Magnesia?—Magnesia dissolves in water through *which seleniuretted hydrogen* is passed. (Berzelius.)

C. Selenite of Magnesia.—*a. Monoselenite.*—Prepared by digesting carbonate of magnesia in an aqueous solution of selenious acid. Granular, or crystallizing by the evaporation of a hot aqueous solution, in small hydrated four-sided prisms and tables (in rhombic prisms, according to Muspratt). When heated, it loses water and assumes an enamel-like appearance; and, in this state, attacks glass like the selenite of lime, but without fusion or loss of acid (after fusion, according to Muspratt). Very slightly soluble in hot water. The crystals contain 3 atoms of water; and the salt is isomorphous with the sulphate and carbonate of the same base. (Muspratt.)

*b. Biselenite.*—Formed by dissolving *a* in excess of selenious acid, and precipitating with alcohol. Uncrystallizable, tenacious, deliquescent mass. (Berzelius.)

D. Seleniate of Magnesia.—Resembling the sulphate in solubility, and in the form of its crystals. (Berzelius, *Lehrb.* 4, 317.)

## Magnesium and Iodine.

A. Hydrated Protiodide of Magnesium, or Hydriodate of Magnesia.—A difficultly crystallizable salt which deliquesces in the air, and, on exposure to heat, gives off hydriodic acid and is converted into pure magnesia.

B. Hypo-iodite of Magnesia ?—When magnesia and iodine are brought together under water, reddish-brown flakes are deposited and a small quantity of iodate and hydriodate of magnesia are found in the solution; these, on evaporating the water, are likewise changed into brownish, insoluble flakes. This brown compound is resolved by heat into magnesia and vapour of iodine. Boiled with a large quantity of water, it is resolved into iodate and hydriodate of magnesia which dissolve, and magnesia which remains as a white precipitate. (Gay-Lussac.)

C. Iodate of Magnesia.—A soluble salt not yet further examined.

## Magnesium and Bromine.

A. Bromide of Magnesium.—Found in sea-water and in numerous salt-springs.—Bromine alone does not decompose magnesia at a red heat. (Balard.) The compound is formed by passing vapour of bromine over a mixture of magnesia and charcoal at a red heat. (Löwig.) A portion of the bromide of magnesium is carried over into the receiver by the carbonic acid gas, another portion remaining at the extremity of the porcelain tube. (Serullas.) White mass, of crystalline aspect; not fusible below a red heat; not volatile. (Serullas, *J. Chim. Med.* 8, 4; also *Pogg.* 24, 343.) The dry salt or a very concentrated solution, evolves bromine immediately on the addition of oil of vitriol; but if it be distilled in a dilute state with sulphuric acid, the whole of the bromine passes over in the form of hydrobromic acid. (Löwig.)

Hydrated Bromide of Magnesium or Hydrobromate of Magnesia.—Bromide of magnesium dissolves in water with evolution of heat

and a hissing noise (Löwig), and deliquesces rapidly in the air. (Serullas.) Magnesia is dissolved in aqueous hydrobromic acid and the solution evaporated to the crystallizing point. This is best accomplished under the evaporating receiver by the aid of oil of vitriol. (Rammelsberg, *Pogg.* 55, 239.) Decomposed by heat into hydrobromic acid gas and magnesia; deliquescent in the air. (Balard.) On distilling the aqueous solution, part of the hydrobromic acid is likewise expelled. (Löwig.)

| | Anhydrous. | | | | Hydrated crystals. | | Rammelsberg. |
|---|---|---|---|---|---|---|---|
| Mg | 12·0 | 13·27 | Mg | 12·0 | 8·31 | 8·74 | |
| Br | 78·4 | 86·73 | Br | 78·4 | 54·29 | 54·00 | |
| | | | 6HO | 54·0 | 37·40 | 37·26 | |
| MgBr | 90·4 | 100·00 | + 6Aq. | 144·4 | 100·00 | 100·00 | |

B. Hypobromite of Magnesia?—Bromine, shaken up with magnesia diffused in water, and filtered, yields a yellowish liquid, which first turns reddened litmus blue and then bleaches it; bromine is evolved on the addition of even the weakest acids. (Löwig.) Light, heat, evaporation in vacuo, or an excess of bromine, decomposes this compound into bromate and hydrobromate of magnesia. (Balard.)

C. Bromate of Magnesia.—Prepared by dissolving pure magnesia or the carbonate in an aqueous solution of bromic acid. (Löwig.) Regular octohedrons containing water; they effloresce in the air and fuse when heated, in their water of crystallization, which is driven off entirely at a temperature above 200° (392° F). On slightly increasing the heat, vapour of bromine and oxygen gas are expelled, and pure magnesia remains behind. Soluble in 1·4 parts of cold water. (Rammelsberg, *Pogg.* 52, 89.)

## Magnesium and Chlorine.

A. Chloride of Magnesium.—Found in sea-water and in several mineral waters and salt-springs. Magnesium takes fire in chlorine gas. (Liebig.) Magnesia absorbs chlorine at a red heat, evolving a quantity of oxygen gas equal to half the volume of the chlorine. (H. Davy.)—1. Prepared by passing chlorine over ignited magnesia. (Gay-Lussac & Thénard.)—2. By passing chlorine over an ignited mixture of magnesia and charcoal, which latter facilitates the decomposition. Bussy (*J. Chim. Med.* 6, 141) mixes equal parts of magnesia and starch with a small quantity of water, and works them well together to the consistence of dough; ignites the mixture thoroughly in a covered crucible; heats the carbonaceous residue to redness in a slightly inclined porcelain tube; and passes chlorine gas over it. The chloride of magnesium runs down the tube without volatilizing.—3. By igniting the double chloride of magnesium and ammonium. (Döbereiner, *Schw.* 28, 90.) Liebig evaporates a solution if equal parts of hydrochlorate of magnesia and sal-ammoniac to dryness; projects the residue in small quantities at a time into a red-hot platinum crucible; and continues the heat till all the sal-ammoniac is expelled, and the mass enters into tranquil fusion. A similar product is obtained by igniting an intimate mixture of 1 part of magnesia with 2 parts of sal-ammoniac. (Berzelius.)

White, translucent mass, consisting of large, flexible, crystalline plates, with a pearly lustre. Fuses by gentle ignition, and forms a clear

liquid. Its taste is sharp and bitter. It may be ignited in a perfectly dry atmosphere, without undergoing decomposition; but when water is present, it is resolved into hydrochloric acid gas and magnesia. (Gay-Lussac & Thénard.) It is decomposed by ignition with chlorate of potash. (Döbereiner, *N. Br. Arch.* 13, 155.) Red oxide of mercury heated in an aqueous solution of this salt precipitates magnesia. (Berzelius.)

| | Calculation. | | |
|---|---|---|---|
| Mg | 12·0 | .... | 25·32 |
| Cl | 35·4 | .... | 74·68 |
| Mg, Cl | 47·4 | .... | 100·00 |

| | Or: | | Wenzel. | | Marcet. | | Berthollet. | |
|---|---|---|---|---|---|---|---|---|
| MgO | 20·0 | 42·19 | 43 | | 43·99 | | 36·5 | |
| $MuO^2$ | 27·4 | 57·81 | 57 | | 56·01 | | 63·5 | |
| MgO, $MuO^2$ | 47·4 | 100·00 | 100 | | 100·00 | | 100·0 | |

*Hydrated Chloride of Magnesium* or *Hydrochlorate of Magnesia.*—Chloride of magnesium evolves considerable heat with water. (Döbereiner.)—1. Magnesia alba is dissolved in dilute hydrochloric acid and the solution evaporated.—2. A solution of 2 parts of sulphate of magnesia and 1 part of common salt in $4\frac{1}{2}$ parts of water is evaporated to 4 parts, and exposed to a temperature of 3° (37·4° F.), whereupon Glauber's salt crystallizes out, and hydrochlorate of magnesia remains in solution. (Berzelius.) Crystallizes with difficulty in needles and prisms; has a sharp bitter taste. The crystals begin to give off hydrochloric acid at 106°; fuse partially at 112°, and completely at 119° (Brandes, *Br. Arch.* 12, 195); and are converted, with loss of water and hydrochloric acid, into a mixture of magnesia with a small quantity of chloride of magnesium. (H. Davy.) The presence of sal-ammoniac (Döbereiner) or of chloride of sodium; (Ligéard, *Br. Arch.* 14, 149)—compounds which have great affinity for chloride of magnesium—prevents its decomposition into hydrochloric acid and magnesia, by evaporation and exposure to a high temperature. The salt is deliquescent in the air; dissolves in 0·6 parts of cold, and in 0·273 parts of hot water; in 5 parts of alcohol of specific gravity 0·90°; and in 2 parts of alcohol of specific gravity 0·817.

| | Crystallized. | | | Graham. |
|---|---|---|---|---|
| Mg | 12·0 | .... | 11·83 | |
| Cl | 35·4 | .... | 34·91 | .... 33·91 |
| 6HO | 54·0 | .... | 53·26 | |
| MgCl + 6Aq. | 101·4 | .... | 100·00 | |

| | Or: | | | Murray. |
|---|---|---|---|---|
| MgO | 20·0 | .... | 19·72 | .... 21·3 |
| HCl | 36·4 | .... | 35·90 | |
| 5HO | 45·0 | .... | 44·38 | |
| MgO, HCl + 5Aq. | 101·4 | .... | 100·00 | |

With hydrochlorate of magnesia, ammonia in excess gives a colourless, opaque, clammy precipitate, which slowly collects at the bottom of the vessel, and, after thorough washing, still retains about one per cent. of hydrochloric acid. (Berzelius.)

B. Hypochlorite of Magnesia.—The earth dissolved in an aqueous solution of hypochlorous acid yields a bleaching liquid, which, when excess of the acid is present, is gradually and spontaneously converted into chlorate and hydrochlorate of magnesia, oxygen and a small quantity of chlorine being set free. If the magnesia is in excess, it is decomposed by evaporation in vacuo. (Balard.) *Chloride of magnesia*—that is to say, the hypochlorite mixed with hydrochlorate of magnesia—is obtained when chlorine gas is passed through water in which magnesia is diffused. The liquid, even after boiling for a quarter of an hour, still retains bleaching properties. (Grouvelle.)

C. Chlorate of Magnesia.—$MgO, ClO^5 + 6Aq$. Hydrofluosilicate of magnesia is added to a boiling aqueous solution of chlorate of potash as long as a precipitate appears; the liquid is then filtered and evaporated to a small bulk. (Berzelius.) This compound forms a thin crystalline crust, and possesses, according to Chenevix, the same characters as the chlorate of lime; according to the same authority, it contains 25·7 per cent. of magnesia, 60·0 of chloric acid, and 14·3 of water. It is readily soluble in alcohol; fuses at 40°; and loses its water at 120°. (Wächter.)

D. Perchlorate of Magnesia.—Long prisms, deliquescent, and soluble in alcohol. (Serullas.)

E. Chloride of Iodine and Magnesium.—1. Iodate of magnesia rubbed down with hydrochloric acid of 22° Bm. to a thin paste, is introduced quickly into a cylindrical vessel surrounded with lukewarm water, and hydrochloric acid gas passed through till every thing is dissolved, and no more chlorine escapes; the liquid is then cooled till crystallization commences.—2. A concentrated solution of hydriodate of magnesia is saturated with chlorine gas.—3. An aqueous solution of terchloride of iodine is mixed with hydrochlorate of magnesia.—Crystals, not distinguishable, either in form or in colour, from the potassium compound, and of similar chemical constitution; very easily decomposed. Deliquescent. (Filhol, *J. Pharm.* 25, 442.)

## Magnesium and Fluorine.

A. Fluoride of Magnesium.—Formed by treating carbonate of magnesia with hydrofluoric acid, or by mixing fluoride of potassium with sulphate of magnesia dissolved in water. White, tasteless, and not decomposed by ignition. (Berzelius.) Insoluble in water, and nearly insoluble in acids (Gay-Lussac & Thénard); not soluble in water, or in excess of aqueous hydrofluoric acid. (Berzelius, *Pogg.* 1, 22.)

B. Hydrofluate of Borate of Magnesia.—Large prisms, of a bitter taste; readily soluble in water. (Berzelius.)

## Magnesium and Nitrogen.

A. Nitrite of Magnesia.—Deliquescent. (Mitscherlich.) Forms a scaly, saline mass, readily soluble in alcohol; insoluble in absolute alcohol. (Fischer, *Pogg.* 74, 115.)

B. Nitrate of Magnesia.—Found in spring-water, though rarely, as in that of Stockholm. (Berzelius.) It is formed in nitre-beds when substances containing magnesia are present. Prepared by dissolving magnesia alba in nitric acid and concentrating by evaporation.—The salt does not give up the whole of its water, even at a temperature between 320° and 400° (608°, 752° F.), not indeed till the acid itself begins to escape (in the form of hyponitric acid and oxygen gas). The decomposition may be completely effected over the flame of a spirit-lamp. (Graham, *Schw.* 55, 195.) The salt detonates slightly with combustible bodies, and is decomposed by an aqueous solution of sulphate of potash into nitrate of potash and sulphate of magnesia, which forms a double salt with the sulphate of potash if the latter is in excess. (Funcke.)

*α. With one atom of Water.*—Prepared by heating the sex-hydrated salt to the melting point of lead. The fused residue is transparent. (Graham, *Ann. Pharm.* 29, 17.)

*β. With 6 atoms of Water.*—Crystallizes, on cooling a concentrated solution. Rhombic prisms and needles, having a sharp bitter taste. The crystals melt in the fire, and lose from 34·02 to 34·26 per cent. (5 At.) of water. (Graham.) They deliquesce rapidly in the air, and dissolve in half their weight of cold water, and in 9 parts of cold alcohol of specific gravity 0·840; with greater difficulty, however, in absolute alcohol (according to John, scarcely at all).

| | Anhydrous. | | Wenzel. | Bucholz. | Richter. | Berthollet. |
|---|---|---|---|---|---|---|
| MgO | 20 | 27·03 | 28 | 30 | 30·45 | 33·6 |
| $NO^5$ | 54 | 72·97 | 72 | 70 | 69·55 | 66·4 |
| MgO, $NO^5$ | 74 | 100·00 | 100 | 100 | 100·00 | 100·0 |

With one atom of water.

| | | |
|---|---|---|
| MgO | 20 | 24·10 |
| $NO^5$ | 54 | 65·06 |
| HO | 9 | 10·84 |
| MgO, $NO^5$ + Aq. | 83 | 100·00 |

| | Crystallized. | | Graham. | Kirwan. | Bergman. |
|---|---|---|---|---|---|
| MgO | 20 | 15·62 | 15·86 | 22 | 27 |
| $NO^5$ | 54 | 42·19 | | 46 | 43 |
| 6HO | 54 | 42·19 | | 32 | 30 |
| MgO, $NO^5$ + 6Aq. | 128 | 100·00 | | 100 | 100 |

The last two formulæ may also be written: MgO, HO, $NO^5$ and: MgO, HO, $NO^5$ + 5Aq.

C. Carbonate of Magnesia and Ammonia.—Crystallizes from a mixture of the cold aqueous solutions of sulphate or hydrochlorate of magnesia and excess of sesqui-carbonate of ammonia, after standing for several hours. (Fourcroy, Bucholz; Gren, *Grundr. d. Chem.* revised by Bucholz, 1, 274.) From 2 to 3 parts of carbonate of ammonia are required for one part of sulphate of magnesia. (Guibourt.) A solution of magnesia in an aqueous solution of sesqui-carbonate of ammonia also yields a crop of crystals after a short time. (Wittstein, *Repert.* 57, 67.) Translucent rhombohedral crystals. (Döbereiner, *Schw.* 13, 320.) They evolve ammonia when exposed to the air. The odour is no longer emitted after they have been thoroughly dried by means of chloride of calcium, but is again evolved when they are wetted. (Guibourt.) The residue, after ignition, consists of magnesia. The crystals are not soluble in aqueous solution of carbonate

of ammonia, but dissolve in pure water without decomposition. The solution, when heated, evolves carbonate of ammonia, and deposits all the magnesia in the form of carbonate. (Guibourt.) If a portion of sulphate of ammonia still adheres to the salt, the precipitate diminishes in quantity on further application of heat. (Guibourt.) According to Bucholz, the crystals are decomposed by water, a salt richer in carbonate of ammonia being dissolved, and a salt containing less of that substance remaining behind.

| | Crystallized. | | | Bucholz. | | Guibourt. |
|---|---|---|---|---|---|---|
| $NH^3$ ..... | 17 | 13·49 | | | | |
| MgO ..... | 20 | 15·87 | .... | 18 | .... | 15·625 |
| $2CO^2$ ..... | 44 | 34·92 | .... | 32 | | |
| 5HO ..... | 45 | 35·72 | $+ NH^3$ | 50 | | |
| | 126 | 100·00 | | 100 | | |

D. Borate of Magnesia and Ammonia.—An aqueous mixture of borate of ammonia and hydrochlorate of magnesia spontaneously evaporated, deposits a crystalline crust containing 2·69 per cent. of ammonia, from 8 to 9 of magnesia, and from 43 to 45 of water, while chloride of ammonium and the excess of borate of ammonia remain in the mother-liquid. An aqueous solution of this salt becomes turbid when boiled, and evolves ammonia. (Rammelsberg, *Pogg.* 49, 451.)

E. Phosphite of Magnesia and Ammonia.—Formed by mixing the solutions of the two simple salts. Crystallizable, and but slightly soluble in water. (Fourcroy & Vauquelin.)

F. Phosphate of Magnesia and Ammonia.—Discovered by Fourcroy.—¶ Found native by Ulex (*Ann. Pharm.* 58, 99), in some old soil in the city of Hamburg, crystallized in regular six-sided prisms with dihedral summits, belonging to the right prismatic system. Some of the crystals were between one and $1\frac{1}{4}$ inch long, and $\frac{1}{4}$ inch thick, and weighed from one to 2 grammes. Sp. gr. = 1·7. Ulex distinguishes this mineral by the name of *Struvite*. ¶ Found likewise in certain animal concretions, and deposited from decomposing urine. It is precipitated from any solution whatever, in which magnesia meets with phosphoric acid and ammonia.—1. Phosphate of magnesia with diphosphate of ammonia. (Fourcroy.) The supernatant liquid becomes acid. (Wach.)—2. A neutral salt of magnesia with diphosphate of ammonia, the solution being heated. (Berzelius.) In this case also the liquid becomes acid. (Wach.)

$$2(MgO, SO^3) + 2NH^3, cPO^5 = NH^3, 2MgO, cPO^5 + NH^3, SO^3 + SO^3.$$

—3. A salt of magnesia with phosphate of ammonia mixed with free ammonia.—4. A salt of magnesia mixed with bicarbonate of ammonia, and then with diphosphate of soda. (Riffault, *Ann. Chim. Phys.* 19, 90; also *N. Tr.* 7, 1, 302.)—5. A salt of magnesia mixed with diphosphate of soda, and then with ammonia. Graham (*Ann. Pharm.* 29, 25) adds to 4 lbs. of hot water containing 200 grs. of ammonia, 350 grs. of ordinary crystallized diphosphate of soda, 100 grs. of salammoniac, and 200 grs. of sulphate of magnesia. The precipitate gradually appears, and the alkaline liquid becomes neutral; if the ammonia be left out, the same precipitate is obtained, but in smaller quantity, and the supernatant liquid becomes acid. The precipitate is well washed with cold water, pressed between blotting-paper, and dried in the air at a temperature of 18°. *(64·4° F.)*

In all these cases, the salt is precipitated by degrees, and the precipitation is never complete unless an excess of the phosphate is present in the solution. (Berzelius.) The salt is deposited on the sides of the glass vessel, especially where the stirring rod has scratched it. (Wollaston.)

White, sandy, crystalline powder, or translucent four-sided prisms, with irregular four-sided summits. Tasteless. Parts with ammonia even at ordinary temperatures on exposure to the air (Pfaff); when dried for several days in vacuo over oil of vitriol, it loses both water and ammonia. (Wach. *Schw.* 59, 290.) Heated in a retort to 100°, it loses 10 atoms of water, but no ammonia. (Graham.) When strongly heated, it loses all its ammonia and water, and is reduced to a powder which fuses before the blowpipe to a clear glass consisting of dipyrophosphate of magnesia. If, when all the water and ammonia have been driven off at a moderate heat, the residue is subsequently exposed to a greater degree of heat, it becomes slightly incandescent. (I. 107.) If the residue be dissolved in nitric acid before incandescence, the solution gives a *yellow* precipitate with nitrate of silver; but if it be not dissolved till after incandescence has taken place, a *white* precipitate is obtained, in consequence of the formation of pyrophosphoric acid. (Berzelius.) (Fourcroy, *Syst. de connaiss. chim.* 3, 268.) The ignited residue amounts, according to Wach, to 44·6 per cent. according to Riffault, to 47·475; and according to Lindbergson, to 62·5 per cent. It contains in 100 parts, 22·26 parts of magnesia, according to Lindbergson; 35·378 parts (Riffault); 36·67 parts (Berzelius); 37 parts (Stromeyer, *Pogg.* 11, 170); and 39 to 43 parts according to Pfaff. According to the calculation given below, 100 parts of the salt yield by ignition 45·39 parts of residue, containing 35·91 per cent. of magnesia, and 64·09 per cent. of phosphoric acid. By igniting the salt with charcoal, a portion of its acid is reduced to phosphorus. The fixed alkalis set the ammonia free; and acids, including acetic and carbonic acid (Pfaff, *Schw.* 36, 431), dissolve the salt readily, with partial decomposition. The solution in hydrochloric acid, evaporated to dryness and heated, yields a sublimate of sal-ammoniac. (Marcet.) The salt is insoluble in water which contains any salt of phosphoric acid whatever, but is slightly dissolved by pure water and by the aqueous solutions of other salts. (Berzelius, *Pogg.* 4, 275.)—¶ One part of the salt dissolves in 15,293 parts of pure water at ordinary temperatures; the solution mixed with ammonia gives, after some time, a distinct crystalline precipitate. One part of the salt dissolves in 44,330 parts of solution of ammonia; in 7,548 parts of chloride of ammonium; and in 15,627 parts of a solution of chloride of ammonium containing free ammonia. (Fresenius, *Ann. Pharm.* 55. 109, 1845.) ¶

| | Calculation. | | Wach. (3.) | (2.) | (1.) |
|---|---|---|---|---|---|
| $NH^3$ ..... | 17·0 | 6·93 | 6·76 .... | 7·15 .... | 7·07 |
| 2MgO ..... | 40·0 | 16·30 | 16·24 .... | 17·04 .... | 17·10 |
| $ePO^5$ ..... | 71·4 | 29·09 | 28·36 .... | 29·75 .... | 29·85 |
| 13HO ..... | 117·0 | 47·68 | 48·64 .... | 46·06 .... | 45·98 |
| | 245·4 | 100·00 | 100·00 .... | 100·00 .... | 100·00 |

| Otto. | Riffault. (4.) | Lindbergson. |
|---|---|---|
| 6·83 .... | 13·88 .... | 11·65 |
| 16·28 .... | 16·81 .... | 14·00 |
| 28·12 .... | 30·67 .... | 48·90 |
| 48·77 .... | 38·64 .... | 25·45 |
| 100·00 .... | 100·00 .... | |

The salt is regarded by Graham as $NH^4O, 2MgO, cPO^5 + 2HO + 10\,Aq$. The oxide of ammonium formed from the elements of ammonia and one atom of water, constitutes the third atom of base; and of the other 12 atoms of water, 2 atoms are more intimately, and 10 atoms less intimately combined. From the analysis of Lindbergson (*Schw.* 30, 437), Berzelius concludes that there likewise exists a more neutral salt, composed of $NH^3, MgO, PO^5 + 4Aq$.—and obtained as a fine, slowly falling crystalline powder on mixing warm solutions of sulphate of magnesia and diphosphate of ammonia; but according to Wach., this precipitate has the composition given under 2. According to Graham, also, there exists but one double salt composed of magnesia, ammonia, and ordinary phosphoric acid. Tünnermann (*N. Tr.* 26, 1, 6) supposes the existence of even six varieties of this salt.

G. Metaphosphate of Magnesia and Ammonia.—Hydrated metaphosphoric acid recently ignited, is dissolved in ammonia—the vessel containing the mixture being kept cool with water, and the solution added to that of sulphate of magnesia. As long as the latter continues in excess, the precipitate first formed is redissolved; but on the addition of a larger quantity of metaphosphate of ammonia, it becomes permanent. Alcohol precipitates the portion which still remains in solution. An excess of hydrochlorate, nitrate, or acetate of magnesia, which gives the same precipitate, does not dissolve it so readily.—Feathery flakes, uniting in a stringy mass like turpentine, which, after being washed with water and dried, becomes transparent and brittle like glass. Heated in a glass tube, it swells up to an opaque spongy mass, and evolves nothing but water at first, but afterwards a large quantity of ammonia. The residue neither becomes incandescent nor fuses at the temperature at which glass softens. It dissolves with difficulty in water, forming a solution which has an acid reaction; it is but slightly soluble in acids. The undecomposed double salt dissolves somewhat freely in cold water, but is precipitated on the addition of alcohol. The cold solution, which exhibits an acid reaction on vegetable colours, deposits the salt on the application of heat, in a mass of the consistence of turpentine, but dissolves it again on cooling. In boiling water, the salt swells up to an opaque frothy mass, but does not dissolve to any considerable extent. (Wach, *Schw.* 59, 297.)

| | Calculation. | | | | Wach. |
|---|---|---|---|---|---|
| $NH^3$ ..... | 17·0 | .... | 3·12 | .... | 3·124 |
| 4MgO ..... | 80·0 | .... | 14·69 | .... | 14·393 |
| $4PO^5$..... | 285·6 | .... | 52·44 | .... | 53·552 |
| 18HO ..... | 162·0 | .... | 29·75 | .... | 28·931 |
| | 544·6 | .... | 100·00 | .... | 100·000 |

The stoïchiometrical relations of this compound do not correspond, either to those of a metaphosphate or to those of a pyrophosphate.

¶ H. Hyposulphite of Magnesia and Ammonia.—Prepared by decomposing the double sulphate with hyposulphite of baryta or strontia, and cooling the filtrate below the freezing point. Very deliquescent crystals. The formula of the salt is $NH^4O, MgO, 2S^2O^2 + 6Aq$. (Kessler, *Pogg.* 74, 274.) ¶

I. Sulphite of Magnesia and Ammonia.—When magnesia is dissolved at a *low temperature* in an aqueous solution of sulphite of

ammonia (at too high a temperature, all the ammonia is expelled), the double salt separates from the solution in shining crystals, nearly tasteless, and but slightly soluble. (Fourcroy & Vauquelin.)

K. Sulphate of Magnesia and Ammonia.—Precipitated as a crystalline powder, on mixing the concentrated solutions of the two simple salts. Crystallizes in large transparent prisms, belonging to the oblique prismatic system (*Fig.* 84), together with the *t* and *h* surfaces; $i : u$ or $u^1 = 104° 45'$ (108° Beudant); $i : a = 154° 40'$; $i : h$ *backwards* $= 135° 40'$; $i : f = 115° 30'$; $u^1 : u = 109° 30'$ (109° Beudant); $u : t = 125° 15'$. (Brooke, *Ann. Phil.* 23, 117.) Sp. gr. = 1·721. (Thomson.) Taste, acrid and bitter. The crystals, when heated, undergo the aqueous fusion and are decomposed. At 132°, they lose all their water, excepting the one atom which belongs to the ammonia. (Graham.) They are less soluble in water than either of the simple salts of which they are composed.

Crystallized, according to Mitscherlich.

| | | | |
|---|---|---|---|
| $NH^3$ | 17 | .... | 9·44 |
| MgO | 20 | .... | 11·11 |
| $2SO^3$ | 80 | .... | 44·45 |
| 7HO | 63 | .... | 35·00 |
| $NH^4O, SO^3 + MgO, SO^3 + 6Aq.$ | 180 | .... | 100·00 |

L. Chloride of Magnesium and Ammonium, and Hydrochlorate of Magnesia and Ammonia.—$NH^4O, 2Mg, 3Cl + 12Aq$. 1. Solutions of hydrochlorate of magnesia and of sal-ammoniac mixed together, soon deposit small crystals of the double salt. (Fourcroy.) 2. Ammonia added in excess to a solution of protochloride of magnesium, precipitates exactly half the base. (Pfaff.) 3. Magnesia shaken up with a cold solution of sal-ammoniac, dissolves with evolution of ammonia. In both cases, the above compound of chloride of magnesium or hydrochlorate of magnesia with sal-ammoniac is the result.—Small crystals, belonging to the oblique prismatic system, having a bitter saline taste, and soluble in 6 parts of cold water. (Fourcroy.) When dried at 100°, the salt loses 4 atoms of water. Fuses when ignited; gives off water and sal-ammoniac, and leaves chloride of magnesium.

M. Nitrate of Magnesia and Ammonia.—Solutions of nitrate of ammonia and nitrate of magnesia deposit, soon after mixture, fine needles having a slightly bitter taste. These crystals, when suddenly heated, exhibit incandescence; but if the temperature be more gradually raised, they fuse and evolve oxygen, nitrogen, hyponitric acid, and water, leaving a residue of magnesia. They attract moisture from the air, dissolve in 10 parts of water at 12·5°, and in a smaller quantity of boiling water. Magnesia, with the aid of heat, expels ammonia from this compound. (Fourcroy, *Ann. Chim.* 4, 215.) Since, according to Pfaff, an excess of ammonia precipitates from neutral nitrate of magnesia no more than one-third of the magnesia, the salt would appear to contain but one atom of nitrate of ammonia to 2 atoms of nitrate of magnesia. Graham (*Ann. Pharm.* 29, 18) did not, however, succeed in preparing this salt, as each *of the simple* salts crystallized separately from the mixed solution.

## Magnesium and Potassium.

A. Magnesia and Potash?—Hydrate of magnesia precipitated by potash retains a portion of the alkali, however long it may be washed. Water dissolves out a compound which contains more potash, deposits magnesia on the application of heat, and then reddens turmeric; but the undissolved portion always retains a small quantity of potash, which, by dissolving in nitric acid, evaporating to dryness, and igniting, may be obtained as nitrite of potash. (Grouvelle, *Ann. Chim. Phys.* 17, 354.)

B. Carbonate of Magnesia and Potash.—Deposited after a few days, in large crystals, from a cold aqueous mixture of hydrochlorate or nitrate of magnesia with excess of bicarbonate of potash. Tasteless at first, but after a few seconds exhibits an alkaline flavour. At 100°, the crystals become opaque and lose water. When strongly heated, they soften and evolve carbonic acid gas in large bubbles; after ignition, a mixture of magnesia and normal carbonate of potash remains. Water dissolves the crystals, but not without decomposition, taking up bicarbonate of potash together with bicarbonate of magnesia, and leaving an insoluble residue of three-fourths carbonate of magnesia. (Berzelius, *Ann. Chim. Phys.* 14, 370.) The portion which remains undissolved after digestion in water, is ter-hydrated monocarbonate of magnesia, mixed with the penta-hydrated salt, the quantity of the latter being greater as the temperature of the water is lower. (Fritzsche.)

| | Crystallized. | | | Berzelius. |
|---|---|---|---|---|
| KO | 47·2 | 18·4 | .... | 18·28 |
| 2MgO | 40·0 | 15·6 | .... | 15·99 |
| $4CO^2$ | 88·0 | 34·4 | .... | 34·49 |
| 9HO | 81·0 | 31·6 | .... | 31·24 |
| $KO,2CO^2+2(MgO,CO^2)+9Aq.$ | 256·2 | .... 100·0 | .... | 100·00 |

Another double carbonate of magnesia and potash is precipitated, together with carbonate of magnesia, on adding an excess of carbonate of potash to the solution of a magnesia salt, at a temperature below the boiling point. It is but slightly soluble in water, and crystallizes from its solution in small grains. If the temperature is raised to ebullition, pure carbonate of magnesia is alone precipitated. (Bonsdorff, *Ann. Chim. Phys.* 20, 12; & *Pogg.* 18, 126.)

C. Borate of Magnesia and Potash?—From an aqueous mixture of one atom of borate of potash and 2 atoms of hydrochlorate of magnesia, chloride of potassium slowly crystallizes: the syrupy mother-liquor solidifies in a crystalline mass. (Rammelsberg.)

D. Hyposulphite of Magnesia and Potash.—The mixed solution of the two salts in equivalent proportion yields, on evaporation, a crystalline mass, which, by rinsing with water and recrystallization, may be purified from excess of the more soluble potash-salt. The crystalline mass does not lose water over oil of vitriol in vacuo; when exposed to the air, it rapidly attracts moisture. (Rammelsberg, *Pogg.* 56, 304.) Fuses and deposits sulphur even below 100°. (Kessler.)

| | Calculation. | | | Rammelsberg. |
|---|---|---|---|---|
| KO | 47·2 | .... | 21·73 | 21·42 |
| MgO | 20·0 | .... | 9·21 | 9·31 |
| $2S^2O^2$ | 96·0 | .... | 44·20 | |
| 6HO | 54·0 | .... | 24·86 | |
| | 217·2 | .... | 100·00 | |

E. Sulphate of Magnesia and Potash.—Found, according to Marcet, in sea-water; also in the mother-liquor of the Lüneburg, and Schönebeck springs. (Busch, Hermann, *Br. Arch.* 28, 257 and 259.) Formed by evaporating the mixed solutions of the two simple salts to the crystallizing point. Hydrated crystals, isomorphous with those of the double sulphate of magnesia and ammonia. (*Fig.* 84.) $i : u^1$ or $u = 102° 20'$; $i : m = 105° 8'$; $i : a = 154° 30'$; $i : f = 116° 45'$; $u^1 : u = 108° 45'$. No plane of cleavage. (Brooke, *Ann. Phil.* 22, 41.) Loses all its water of crystallization a little above 132° (269·6° F.). (Graham.) Soluble in water.

Crystallized, according to Mitscherlich.

| | | | |
|---|---|---|---|
| KO | 47·2 | .... | 23·46 |
| MgO | 20·0 | .... | 9·94 |
| $2SO^3$ | 80·0 | .... | 39·76 |
| 6HO | 54·0 | .... | 26·84 |
| $KO,SO^3 + MgO,SO^3 + 6Aq.$ | 201·2 | .... | 100·00 |

According to Pfaff and Van der Smissen (*Schw.* 45, 380), sulphate of potash unites with the sulphate of magnesia in different proportions, giving rise to differently formed crystals. Thus, Link obtained long prisms which crumbled in the air; Berthollet, permanent rhombohedral crystals.

F. Hydrated Bromide of Magnesium and Potassium, or Hydrobromate of Magnesia and Potash.—A dilute aqueous mixture of the two simple salts evaporated in the air, yields large, transparent, right rhombic prisms having a cooling bitter taste, like that of borax; they are permanent in the air. When heated, they fuse in their own water of crystallization. Alcohol separates the bromide of magnesium, leaving the bromide of potassium unacted on. The crystals are very soluble in water; the solution evaporated between 75° and 87° (167° to 188·6° F.), deposits crystals of bromide of potassium, and retains the bromide of magnesium in solution. (Löwig, *Repert.* 29, 261.)

| | Crystallized. | | | Löwig. |
|---|---|---|---|---|
| K | 39·2 | 14·96 | .... | 15·65 |
| Mg | 12·0 | 4·58 | .... | 4·70 |
| 2Br | 156·8 | 59·85 | .... | 58·60 |
| 6HO | 54·0 | 20·61 | .... | 21·05 |
| KBr, MgBr + 6Aq. | 262·0 | .... 100·00 | .... | 100·00 |

G. Hydrated Chloride of Magnesium and Potassium, or Hydrochlorate of Magnesia and Potash.—Crystallizes from the last mother-liquor of sea-water, by careful evaporation, in rhombohedral crystals (Marcet), and from the mother-liquor of the Salzhausen spring, during the cold of winter, in irregular octohedrons with truncated vertices. (Liebig, *Kastn. Arch.* 9, 316.) It deliquesces in the air, forming a solution of hydrochlorate of magnesia, while chloride of potassium remains

undissolved. (Liebig.) Alcohol also withdraws hydrochlorate of magnesia from the crystals, leaving chloride of potassium; they are also resolved into the two simple salts by solution in water.

| | Crystallized. | | Or: | | | Liebig. |
|---|---|---|---|---|---|---|
| K | 39·2 | 14·13 | KO | 47·2 | 17·01 .... | 16·30 |
| 2Mg | 24·0 | 8·65 | 2MgO | 40·0 | 14·42 .... | 14·05 |
| 3Cl | 106·2 | 38·29 | 3HCl | 109·2 | 39·37 .... | 37·65 |
| 12HO | 108·0 | 38·93 | 9HO | 81·0 | 29·20 .... | 30·01 |
| KCl, 2MgCl + 12Aq. | 277·4 | 100·00 | | 277·4 | 100·00 .... | 98·01 |

## Magnesium and Sodium.

A. Magnesia and Soda?—Similar to the compound of magnesia and potash. (Grouvelle.)

B. Carbonate of Magnesia and Soda.—*a.* An aqueous solution of the hydrochlorate or nitrate of magnesia mixed with excess of bicarbonate of soda, yields crystals similar to those obtained with bicarbonate of potash, but not so easily decomposed by water. (Berzelius.)

*b.* When a magnesia-salt is precipitated by carbonate of soda in excess (the liquid being heated), a coarse-grained compound is formed, consisting of 100 parts of carbonate of magnesia with 26 parts of carbonate of soda, and slightly soluble in water as a whole, without separation of the soda-salt. (Mosander, *Pogg.* 5, 505.) If the carbonate of magnesia in the compound is decomposed by ignition, the carbonate of soda may then be dissolved out by water. (Berzelius, *Lehrb.* 4, 311.)

Magnesia ignited with 2 parts of carbonate of soda, forms a white, opaque, friable, and ill-combined mass. (Morveau.) Perfect combination does not take place even in the blowpipe flame.

C. Borate of Magnesia and Soda.—A cold aqueous mixture of sulphate of magnesia and borax deposits—after standing for some months—first, needles of borate of magnesia (III., 231, *b.*), and subsequently, double borate of magnesia and soda in large transparent, colourless, shining crystals, belonging to the oblique prismatic system. (Wöhler, *Pogg.* 28, 526.) With 3 parts (2 At.) of borax to one part (1 At.) or 2 parts (2 At.) of sulphate of magnesia, borax crystallizes out first, and then the double salt; a syrupy liquid remains, mixed with crystals of sulphate of soda. [With equal parts of borax and sulphate of magnesia, borax also separates first.] With 3 parts (one At.) of borax to 4 parts (2 At.) of sulphate of magnesia, a large quantity of the double salt is formed; the mother-liquor still retains portions of the double salt, since it becomes turbid when heated; and also sulphate of magnesia, since potash gives a precipitate. (Rammelsberg.) If the double salt were composed of $NaO, 2BO^3 + 2(MgO, 2BO^3)$, the following interchange of elements might be supposed to take place:

$$3(NaO, 2BO^3) + 2MgO, SO^3 = NaO, 2BO^3 + 2(MgO, 2BO^3) + 2(NaO, SO^3);$$

since, however, according to Rammelsberg, the double salt contains one atom less of boracic acid, one atom of that acid must be set free, or a different compound must be produced.—Large, highly lustrous, oblique rhombic prisms. *Fig.* 99 with the *h*-faces; $u : u^1 = 85° 30'$; $a : a^1 = 89°$. (Rammelsberg, *Pogg.* 49, 451.)

| | Crystallized. | | Rammelsberg. | Wöhler. |
|---|---|---|---|---|
| NaO ..... | 31·2 | 6·06 | .... 6·14 | |
| 2MgO ..... | 40·0 | 7·76 | .... 8·44 | |
| $5BO^3$ ..... | 174·0 | 33·77 | .... 34·35 | |
| 30HO ..... | 270·0 | 52·41 | .... 51·07 | .... 52·5 |
| | 515·2 | .... 100·00 | .... 100·00 | |

The crystals effloresce slightly in the air. (Rammelsberg.) When heated, they lose water and swell up, but less strongly than borax. The ignited mass redissolves almost entirely, though very slowly, in cold water; the insoluble residue appears to be triborate of magnesia. A crystal thrown into boiling water becomes opaque; and if it be taken out immediately, before it is reduced to powder, its interior is found to contain a tenacious, stringy mass. The salt is about as soluble in cold water as borax; the solution is not precipitated by ammonia; when heated, it becomes turbid, and deposits triborate of magnesia, which however is again completely dissolved on cooling. When a solution of 100 parts of the crystals is boiled for half an hour and filtered boiling hot, the precipitated borate of magnesia, after being washed and ignited, amounts to 9·8 parts. The filtrate, after evaporation, deposits a crystalline mass of salt which has no alkaline reaction, and yields free boracic acid when digested in alcohol. (Wöhler.)

Hydrate of magnesia also gives with solution of borax a solution which becomes very turbid on the application of heat. When magnesia is dissolved in a boiling aqueous solution of boracic acid, and borax afterwards added, the mixture likewise gives a precipitate every time it is heated, and the precipitate again disappears as the liquid cools. The liquid after evaporation deposits small, difficultly soluble crystals, possessing characters similar to those of the above double salt. (Wöhler.)

By allowing an aqueous mixture of borax with excess of sulphate of magnesia to evaporate spontaneously, Gmelin obtained large, transparent, irregular tetrahedrons, consisting of sulphuric acid, boracic acid, magnesia and soda; a cold aqueous solution of these crystals was rendered turbid by heat, and became clear again on cooling; the author regarded them as a quadruple salt. (*Schw.* 15, 261.) Later experiments, however, convinced him that they were really crystals of sulphate of magnesia (*Fig.* 72), with the *u*-surfaces predominating—which would produce a tetrahedral form—and contaminated with borate of magnesia and soda. By repeated crystallization, the crystals were obtained free from boracic acid and soda. Those obtained with excess of borax doubtless consisted of borate of magnesia and soda, contaminated with sulphate of magnesia. A mixture of chloride of magnesium and borax also becomes turbid when heated, but does not recover its original transparency on cooling.

One part of magnesia ignited with 2 parts of borax forms a hard, translucent, milky glass. (Morveau.)—Before the blowpipe, magnesia behaves with borax like lime; but the compound is not so much inclined to become crystalline. (Berzelius.)

¶ D. Pyrophosphate of Magnesia and Soda.—Prepared like the baryta-salt. Contains between 9·9 and 11·8 per cent. of soda. (Ludwig.)

E. Metaphosphate of Magnesia and Soda.—Discovered accidentally by Gregory in the preparation of phosphoric acid. Insoluble in hydrochloric acid and aqua regia, but dissolved by concentrated sulphuric acid. Composed of $3(MgO, PO^5) + NaO, PO^5$. (Maddrell, *Mem. Chem. Soc. London*, 3, 273, 1848.) ¶

Magnesia unites on ignition with 2 parts of phosphate of soda and ammonia, forming a white, slightly vitrefied substance. (Morveau.) Before the blowpipe, magnesia readily dissolves in phosphate of soda and ammonia, forming a clear bead, which, when not saturated with magnesia, becomes milk-white by interrupted blowing; but if it be saturated with magnesia, the milkiness does not appear till it cools. (Berzelius.)

F. Sulphate of Magnesia and Soda.—¶ Prepared by mixing the two salts in equivalent proportions, and evaporating the mixture at a temperature of 50°. The salt crystallizes in combination with 4 atoms of water. (Arnott, *Phil. Mag.* 3, 24, 502.) ¶ Forms prisms having a bitter taste, and crumbling to powder when exposed to the air. (Link, *Crell. Ann.* 1796, 1, 30.) Transparent, tolerably regular rhombohedrons, with truncated edges and summits; bitter; permanent in the air; when heated, they decrepitate without fusing; soluble in 3 parts of cold water. (Murray.)

| | Anhydrous. | | Link. | Murray. |
|---|---|---|---|---|
| $NaO,SO^3$ | 71·3 | 54·3 | 45·4 | 55 |
| $MgO,SO^3$ | 60·0 | 45·7 | 54·6 | 45 |
| $NaO,SO^3 + MgO,SO^3$ | 131·3 | 100·0 | 100·0 | 100 |

| | Crystallized. | | Murray. |
|---|---|---|---|
| $NaO,SO^3$ | 71·2 | 38·44 | 39 |
| $MgO,SO^3$ | 60·0 | 32·40 | 32 |
| 6HO | 54·0 | 29·16 | 28 |
| + 6Aq. | 185·2 | 100·00 | 99 |

¶ G. Chloride of Magnesium and Sodium.—Poggiale (*Compt. rend.* 20, 1180; also *Ann. Pharm.* 56, 243) mentions a compound of chloride of magnesium with chloride of sodium, the formula of which is $NaCl\,2MgCl + 2HO$. ¶

## Magnesium and Barium.

Magnesia with Baryta.—*a*. The two bodies ignited together in equal weights yield a colourless, irregular, shining mass. (Morveau.)

*b*. Hydrate of magnesia precipitated by baryta contains about 4 per cent. of baryta. (Grouvelle.)

## Magnesium and Calcium.

A. Magnesia with Lime.—Equal weights of the two substances unite on ignition, and form a white, semi-vitrefied mass. (Morveau.)

B. Carbonate of Magnesia and Lime.—Found in the mineral kingdom as *Bitterspar*, *Miemite*, *Dolomite*, and *Bitter-kalk*. Obtuse rhombohedrons, *Fig.* 141; $r^3 : r^5 = 106°\ 55'$ (Malus); $107°\ 22'$ (Mohs): sp. gr. = 2·884 (Mohs). ¶ Kühn (*Ann. Pharm.* 59, 363) describes another native compound of this nature under the name of *Tharandite*, and also varieties of *Bitter-spar*, of a brownish-white colour and fibrous structure, from Bilin. ¶

| | Calculation. | | Klaproth. *Bitter spar.* | Klaproth. *Dolomite.* | Hermann. *Dolomite.* |
|---|---|---|---|---|---|
| $CaO, CO^2$ | 50·0 | 54·35 | 52·0 | 52·00 | 54·6 |
| $MgO, CO^2$ | 42·0 | 45·65 | 45·0 | 46·50 | 45·4 |
| Foreign matters | | | 3·0 | 0·75 | |
| $CaO, CO^2 + MgO, CO^2$ | 92·0 | 100·00 | 100·0 | 99·25 | 100·0 |

Kühn.

| | *Tharandite.* | *Bitter spar.* |
|---|---|---|
| $CaO, CO^2$ | 54·76 | 85·84 |
| $MgO, CO^2$ | 42·10 | 10·39 |
| $FeO, CO^2$ | 4·19 | 5·53 |
| | 101·05 | 101·76 |

Many varieties of Bitter spar, as that of Guhrhofian, consist of: $2(CaO, CO^2) + (MgO, CO^2$; other varieties, including Dolomite, are represented by: $3(CaO, CO^2) + 2(MgO, CO^2)$. The formula for Conite is: $CaO, CO^2 + 3(MgO, CO^2)$; that of Tharandite: $CaO, CO^2 + MgO, CO^2$; and that of Bitter spar from Bilin: $5(CaO, CO^2) + MgO, CO^2$. ¶

C. Hydrated Borate of Magnesia and Lime.—Exists in nature as *Hydroboracite*. White, transparent, of radiating foliated structure; specific gravity about 1·9. Fuses readily, with considerable loss of water, to a clear glass, imparting at the same time a greenish colour to the blowpipe flame. Yields borate of magnesia to boiling water, imparting to it an alkaline reaction. Very soluble in warm hydrochloric acid. (Hess, *Pogg.* 31, 49.)

| | Calculation. | | Hess. |
|---|---|---|---|
| CaO | 28·0 | 13·57 | 13·74 — 13·30 |
| MgO | 20·0 | 9·69 | 10·71 — 10·45 |
| $3BO^3$ | 104·4 | 50·58 | 49·22 — 49·92 |
| 6HO | 54·0 | 26·16 | 26·33 — 26·33 |
| | 206·4 | 100·00 | 100·00 „ 100·00 |

The formula given by Hess: $3CaO, 4BO^3 + 3MgO, 4BO^3 + 9$ [18] Aq. does not accord so well with his own analysis.

D. Nitrate of Magnesia and Lime.—On mixing concentrated solutions of nitrate of magnesia and nitrate of lime, a very insoluble double salt is deposited. (Bergman.)

E. A mixture of 212·8 parts (4 At.) of dry *carbonate of soda* and 92 parts (1 At.) of dolomite, fuses completely at a red heat, and solidifies on cooling to a clear, homogeneous mass of laminated crystalline fracture. If a very strong heat be applied, carbonic acid is evolved; and with a smaller proportion of carbonate of soda, this effect takes place as soon as the mixture begins to soften. (Berthier, *Ann. Chim. Phys.* 38, 249.)

## Magnesium and Magnesium.

*Wagnerite* is a compound of basic phosphate of magnesia with fluoride of magnesium. (Fuchs, *Schw.* 33, 269.) ¶ Its formula is $MgF + 3MgO, PO^5$; it also contains a small quantity of protoxide of iron, replacing magnesia, and traces of silica, lime, and alumina. (Rammelsberg, *Pogg.* 64, 251 and 405; *Ann. Pharm.* 56, 210.) ¶

Magnesium likewise combines with mercury.

# CERIUM.

Klaproth. Ochroit. *A. Gehl.* 2, 303.
Hisinger & Berzelius. Oxides of Cerium. *A. Gehl.* 2, 397.
Vauquelin. Cerite. *A. Gehl.* 5, 189.
Laugier. Cerium and the Oxides of Cerium. *Ann. Chim.* 89, 306; also *Schw.* 19, 54.
Hisinger. Oxides of Cerium. *Schw.* 17, 424; also *Ann. Chim.* 94, 108.
Thomson. *Gilb.* 44, 123.
Gahn & Berzelius. Separation of Cerium from Yttria. *Schw.* 16, 248.
Mosander. Metallic Cerium and its Sulphide. Berzelius, *Lehrb.* 1826, 2, 416; also *Kastn. Arch.* 10, 470; and *Pogg.* 11, 406.
Beringer. Cerium and Ceric oxide. *Ann. Pharm.* 42, 134.
Watts. On Phosphocerite, and on the separation of Cerium, Lanthanum, and Didymium. *Qu. J. of Chem. Soc.* 2, 131.

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*Cerer, Cererium, Cérium.*

*History.* The oxides of Cerium were discovered in 1803, simultaneously by Klaproth and by Hisinger & Berzelius.

*Sources.* Very rare: occurs in native carbonate of protoxide of cerium, in Edwardsite, and in Monazite (phosphate of the protoxide); in Cryptolite and Phospho-cerite; in the neutral and basic fluorides of cerium, and in Yttro-cerite—with silica, &c., in Cerite, Allanite, Orthite, Pyrorthite, and Gadolinite—with titanic acid, &c., in Æschinite, Mosandrite, and Polymignite—with tantalic acid, &c., in Euxenite, Fergusonite, and Pyrochlorite—also in Mikrolite and Tschewkinite.

*Preparation.*—1. Chloride of cerium free from protoxide and from water is decomposed by potassium, with the aid of heat, and the chloride of potassium formed is dissolved out by alcohol or water. (Mosander.) To obtain pure chloride of cerium, dry chlorine gas is passed over sulphide of cerium contained in a glass tube about ten inches long; and, when all the air has been driven out, the tube is heated in the flame of a spirit lamp till decomposition commences with incandescence, which then continues without further application of heat to the tube. When the action has ceased, the chloride of sulphur is expelled from the tube by heating it in a current of chlorine gas, and the chlorine driven out by a current of dry hydrogen gas. A piece of potassium is then put into the nearer end of

the tube, and heat applied—gently at first—the current of hydrogen being constantly kept up, in order to drive out the vapour of rock-oil adhering to the potassium. Afterwards, both the potassium and the chloride of cerium near it are heated more strongly, so that the potassium vapour taken up by the hydrogen may be carried over to the chloride of cerium. Decomposition then takes place, attended with gentle ignition; but if the potassium is too rapidly volatilized, the mass becomes vividly incandescent, and slight explosions are produced. As often as the supply of potassium is exhausted, a fresh portion is introduced, after the tube has cooled; and the operation is continued in this manner till the potassium vapour passes through the tube unchanged. When cold, the tube is cut in two, so that the carbonaceous residue from the potassium may not mix with the cerium. From the dark-brown mass thus produced, the chloride of potassium is dissolved out with alcohol of specific gravity 0·85; and the cerium rapidly washed and dried. If the mass is exhausted with water instead of alcohol, it evolves hydrogen gas; and a portion of hydrated protoxide of cerium is formed which remains mixed with the cerium. Chloride of cerium containing protoxide yields no metallic cerium when acted upon by potassium; the operation likewise fails, if the chloride retains a small quantity of water; in the latter case, potassium gives rise to an explosive action, and the residue contains a mixture of chloride and protoxide of cerium. (Mosander.)—2. Chloride of cerium prepared with sal-ammoniac, (according to the second method p. 270,) is decomposed by potassium or sodium without incandescence. A globule of sodium is introduced into the closed end of a strong glass tube—then a small quantity of chloride of cerium—upon this, another globule of sodium—and so on. The tube is heated in a charcoal fire, till it begins to soften, then allowed to cool, and afterwards divided into several pieces. These are thrown into a glass of cold water; and the cerium, which falls down as a heavy grey powder, repeatedly washed with cold water free from carbonic acid. The flakes of oxidized cerium formed during this process are removed by elutriation; and lastly, the pure cerium is washed with alcohol and rapidly dried. (Beringer.)

Ceric oxide exposed in a charcoal crucible to the strongest heat of a blast-furnace, yields no metal, but only protoxide of cerium. (Mosander, Beringer.)

Vauquelin, by heating tartrate of protoxide of cerium to whiteness in a charcoal crucible, obtained an alloy of cerium with iron, in small white metallic-looking grains, harder and more brittle than cast iron, and of a lamellated texture. The quantity was so small as to lead Vauquelin to suspect that the greater part of the cerium had been volatilized; this property of the metal, which was questioned by Sir H. Davy and Laugier, appears to be confirmed by Thomson and Children (*Ann. Phil.* 2, 147; also *Schw.* 13, 108), who completely volatilized oxalate of cerium by exposing it in a charcoal crucible to the heat of a blast-furnace.

By igniting formiate of protoxide of cerium in a glass tube before the blowpipe, Göbel (*Schw.* 67, 78) obtained cerium contaminated with but a small quantity of protoxide. It formed a steel-grey, coherent mass; and was reduced by trituration to a grey powder, which, under the burnishing-steel, acquired metallic lustre here and there. It was not soluble in hot hydrochloric or nitric acid, but dissolved in aqua regia. According to Beringer, this method yields no metal whatever.

Clarke, with his oxy-hydrogen blowpipe, obtained a very hard bead, of the colour of iron.

*Properties.* Grey powder, resembling pulverized spongy platinum; acquires metallic lustre under the burnishing-steel. (Beringer.) Dark reddish-brown powder, which, under the burnishing-steel, acquires a dull metallic lustre and greyish colour. The powder assumes a more decided rose-colour in proportion to the quantity of protoxide and oxychloride of cerium which it contains. (Mosander.)

¶ *Atomic weight of Cerium:* 46·16 (Beringer); 45·8 (Rammelsberg); 46·0 (Hermann); 47·26 (Marignac, *Arch. Ph. Nat.* 8, 265; *Ann. Pharm.* 58, 212). ¶

## *Compounds of Cerium.*

### Cerium and Oxygen.

### A. Protoxide of Cerium or Cerous Oxide. CeO.

*Ceroxydul, Cereroxydul, White Oxide of Cerium.* (Klaproth's *Ochroit-erde.*)

*Formation.* Cerium decomposes cold water very slowly, and like manganese, causes an evolution of hydrogen gas having a fœtid odour; hence it emits a disagreeable smell when exposed to the air. Water at 90° or 100° degrees is decomposed by it, with rapid evolution of gas. (Mosander.) The product of this action is hydrated ceroso-ceric oxide. (Beringer.) [or rather, perhaps, hydrated cerous oxide, which is raised to a higher degree of oxidation by the oxygen of the air?] Cerium dissolves rapidly in acids, even when very dilute, hydrogen gas being evolved and a cerous salt formed. It likewise evolves hydrogen with oil of vitriol, though much more abundantly on the addition of water. (Mosander.) Sesquioxide of cerium exposed in a charcoal crucible to the strongest heat of a wind-furnace, bakes together to a mass of protoxide, which, under the microscope, exhibits small, yellowish, transparent particles. (Beringer.) Cerium is not reduced to the metallic state from any of its oxides either by charcoal at the heat of a blast-furnace, or by hydrogen gas mixed with potassium vapour at a strong red heat. (Mosander.)

Calculation, according to Hisinger.

| | | | |
|---|---|---|---|
| Ce | 46 | .... | 85·19 |
| O | 8 | .... | 14·81 |
| CeO | 54 | .... | 100·00 |

CeO = 574·7 + 100 = 674·7. (Berzelius.)

*Combinations.* *a.* With water. Hydrate of Protoxide of Cerium. Hydrated Cerous Oxide, Cerous Hydrate.

*Preparation.* *a. From Cerite.*—1. Klaproth boils powdered cerite with 5 parts of aqueous hydrochloric acid; evaporates the solution to dryness in order to separate the silica; redissolves in water, neutralizes the filtrate exactly with ammonia; then throws down the sesquioxide of iron with succinate of ammonia; filters, and precipitates the hydrated cerous oxide by ammonia.—2. Hisinger & Berzelius evaporate to dryness a solution of calcined cerite in aqua regia; exhaust the residue with water; precipitate the filtrate by ammonia; dissolve the washed precipitate in nitric acid; neutralize the liquid with potash, and throw down tartrate of cerium by the addition of neutral tartrate of potash. The tar-

trate of cerium, after being washed and dried, and then ignited in a covered crucible, leaves a residue of ceroso-ceric oxide, from which, by digesting in an acid and precipitating with ammonia, the hydrated protoxide may be obtained.—3. Berzelius evaporates to dryness a solution of ignited cerite in aqua regia; gently heats the residue; exhausts with water; separates the sesquioxide of iron by means of benzoate of ammonia; filters; precipitates by ammonia in excess; dissolves the precipitated hydrate of ceroso-ceric oxide in hydrochloric acid; evaporates the solution to dryness in a retort; and ignites the residue as long as chlorine gas is given off. The protochloride of cerium thus obtained is dissolved in water, and the hydrated protoxide precipitated by potash.—4. Laugier digests cerite in aqua regia; evaporates to dryness; dissolves in water; filters; throws down protoxide of cerium and sesquioxide of iron by ammonia; and treats the precipitate with oxalic acid in excess, which dissolves the oxide of iron completely, but forms with the protoxide of cerium an insoluble compound, from which the hydrated protoxide of cerium may be separated by ammonia.—5. Beringer dissolves cerite in hot aqua regia, evaporates to dryness; exhausts the residue with water; precipitates copper and bismuth, by a current of sulphuretted hydrogen; passes chlorine through the filtrate, to convert the protoxide of iron into sesquioxide; neutralizes with carbonate of soda; mixes the liquid with acetate of soda, and boils till all the iron is precipitated; filters again; and precipitates the hydrated protoxide of cerium by ammonia, leaving lime and cobalt in solution.—6. Persoz (*Ann. Chim. Phys.* 58, 202) frees the protoxide of cerium from sesquioxide of iron by boiling the neutral hydrochloric acid solution with oxide of copper, which throws down the sesquioxide of iron alone; separates the copper by passing sulphuretted hydrogen through the filtrate; and precipitates the cerium, by adding ammonia to the filtered liquid [after expelling the excess of hydrosulphuric acid by heat].—7. On the same principle, Demarçay (*Ann. Pharm.* 11, 245) precipitates the sesquioxide of iron by means of carbonate of baryta, in the cold; then throws down the baryta from the filtrate with sulphuric acid; filters again; and precipitates the protoxide of cerium by the addition of carbonate of potash.—8. In order that cerite may be completely decomposed by aqua regia, it must be very finely divided, and moreover digested repeatedly with fresh quantities of the acid mixture. On this account, oil of vitriol is preferable; but it must be added in large excess at once, otherwise the mixture will become very hot, and the acid will unite with the mineral, forming a hard stony mass, on which water exerts scarcely any action. The powdered cerite is therefore heated with excess of oil of vitriol for several hours; and, after cooling, the sulphates are dissolved out with cold water: if hot water were used, a difficultly soluble sulphate of cerous oxide would be thrown down. The liquid is then filtered, and, without neutralizing the filtrate, a crystalline mass of sulphate of potash is suspended in it, till it becomes saturated in the cold; the double sulphate of cerous oxide and potash which subsides, is then collected on a filter, and washed with a cold saturated solution of sulphate of potash. The double salt is then either fused with carbonate of soda, after which, water dissolves out the sulphate of potash and soda, leaving insoluble ceric oxide; or it is mixed with charcoal and exposed to a white heat, whereby sulphide of potassium and sulphide of cerium are obtained: the sulphide of potassium is then separated from the residue by digestion in water; the sulphide of cerium dissolved in dilute nitric acid; the liquid evaporated to dryness, and the residue ignited: the product is sesquioxide of cerium, mixed with

a variable quantity of protoxide. (Beringer.) Marx (*Schw.* 52, 481) recommends that the cerite be ignited before digestion in sulphuric acid; because it is thereby disintegrated, and afterwards dissolves with greater facility.—¶ 9. Marignac (*Ann. Pharm.* 8, 265) mixes pounded cerite with oil of vitriol in a porcelain basin, so as to form a thick paste, and then applies a gentle heat. A violent action immediately takes place; the mass becomes very hot, turns white, and gives off a portion of the sulphuric acid; so that after a few minutes, a dry white powder is left behind. This is put into an earthen crucible and kept for some time at a heat below redness. It is then left to cool, and afterwards diffused through cold water, care being taken to introduce it only by small portions at a time, as otherwise it will become heated and cake together. The sulphate of cerium then dissolves, while the silica and oxide of iron are left behind, and may be separated by filtration. If the filtrate be then boiled, the cerium will be precipitated in the form of a subsulphate; and from this the oxides may easily be obtained.

*b. From Phosphocerite.* The mineral is finely pounded and boiled with moderately strong sulphuric acid till the whole is reduced to a pasty mass. This mass, when cold, is digested in water; the clear liquid poured off; the insoluble residue again boiled with sulphuric acid, and the treatment repeated till nothing but a small quantity of silica remains behind. The solution is then mixed with ammonia in sufficient quantity to neutralize the greater part of the acid, and the cerium, &c. precipitated by oxalate of ammonia. The precipitated oxalate of cerium, &c., which forms a dense crystalline powder, is then washed, dried, and ignited, whereby it is converted into ceric oxide (mixed with the oxides of lanthanum and didymium) forming a powder of a dark brown-red or tile-red colour. This substance readily dissolves in hot hydrochloric acid, with evolution of chlorine, forming a solution of protochloride of cerium; and from this the protoxide may be obtained by precipitation with caustic potash. (W.) ¶

The hydrated protoxide of cerium prepared by either of these methods contains about 40 per cent. of oxide of lanthanum, together with oxide of didymium. To separate the oxide of lanthanum, the whole is dissolved in nitric acid; the solution evaporated to dryness; and the residue ignited till the nitric acid is wholly expelled. The mixture of ceric oxide and the oxides of lanthanum and didymium which remains, is digested for some hours at a gentle heat, with a mixture of 1 part of nitric acid and from 50 to 100 parts of water. The oxide of lanthanum then dissolves (together with a minute quantity of ceric oxide) and leaves the ceric oxide undissolved, together with the oxide of didymium and a very small quantity of oxide of lanthanum. (Mosander.) The separation is but imperfectly effected, because the precipitated mixture of oxides often contains a small quantity of basic salt or alkaline salt. For this reason, the ceric oxide, freed from the greater part of the lanthanum by nitric acid, must be dissolved in hydrochloric acid; the solution neutralized as exactly as possible with ammonia; acetate of ammonia added; and the protoxide of cerium thrown down by oxalate of ammonia. The oxalate of cerium is then to be collected on a double filter (it would run through a single one*),

* I have never found the slightest difficulty in collecting or washing the precipitated oxalate of cerium, whether pure or mixed with lanthanum and didymium. The precipitate is curdy when first formed, but in a few minutes becomes very dense and crystalline, and may then be washed with the utmost ease, either on the filter or by decantation. [W.]

afterwards washed, dried, and ignited; and the ignited residue again treated with dilute nitric acid to dissolve the remaining portion of oxide of lanthanum. (Th. Scheerer, *Pogg.* 56, 408.)

¶ (*a.*) The separation of cerium from lanthanum and didymium depends upon this circumstance: that cerium forms two oxides, the protoxide or *cerous oxide*, and the sesquioxide or *ceric oxide*, the latter of which is nearly insoluble in weak acids, whereas the oxides of lanthanum and didymium are easily soluble in dilute acids. Moreover, the oxide of lanthanum dissolves more readily than the oxide of didymium, especially when the acid is very dilute and kept quite cold. Hence, when the mixed oxides are treated with cold dilute nitric acid, and for a short time only, the greater part of the lanthanum dissolves, together with small quantities only of cerium and didymium. But if the digestion be long continued—and more especially if it be aided by a gentle heat, and the liquid poured off from time to time, and fresh acid supplied—nearly the whole of the didymium will be removed as well as the lanthanum, and the remaining ceric oxide will be nearly pure, containing but very small quantities of the other oxides. To obtain the ceric oxide quite pure, Marignac (*Ann. Pharm.* 68, 213) digests the residue with moderately strong nitric acid, which dissolves the last traces of lanthanum and didymium, together with a small quantity of cerium.—There is one inconvenience attending this mode of separating cerium from its allied metals, viz., that the ceric oxide when digested in the acid liquid, becomes so minutely divided, that it diffuses itself through the liquid, and will not separate for days; and if an attempt be made to filter the liquid and wash the ceric oxide with water, it first runs through the filter and then completely stops it up. These inconveniences may be obviated to a considerable extent by warming the liquid, and mixing sal-ammoniac or nitrate of ammonia with the water used in washing: the ammoniacal salt may be afterwards expelled by ignition. When all traces of lanthanum and didymium have been thus removed, the residual oxide of cerium may be ignited to expel nitric acid and ammoniacal salt; the residue is ceroso-ceric oxide of a pale yellow colour. By boiling this oxide in a mixture of strong sulphuric and hydrochloric acid (it is insoluble in hydrochloric acid alone) till the liquid becomes colourless and no longer evolves chlorine, a solution of sulphate of cerous oxide is obtained; and when this is mixed with excess of caustic potash, the protoxide of cerium or cerous oxide is precipitated. (W.)

(*b.*) Another mode of separating cerium from lanthanum and didymium is to convert the mixed oxides of the three metals into chlorides (*e. g.*, by treating the crude red-brown oxide of cerium with hot strong hydrochloric acid, in which it easily dissolves, with evolution of chlorine); precipitating with a large excess of caustic potash; and subjecting the precipitate suspended in the liquid to the action of a stream of chlorine gas. The oxides of lanthanum and didymium then dissolve in the mixture of chloride of potassium, hypochlorite of potash, and free hypochlorous acid produced, while the cerium is converted into ceric oxide and remains undissolved. The precipitate first assumes a violet colour, then becomes yellow, and ultimately of a deep orange colour. When this has taken place, the liquid is found to be completely saturated with chlorine, and has acquired a yellow colour. The whole is then set aside for 24 hours in a close vessel, and afterwards the liquid separated by filtration from the insoluble ceric oxide. This is the method by which Mosander first effected the separation of these oxides (*Phil. Mag. J.* 28, 241). According to his statement, the ceric oxide thus obtained is quite free from lanthanum

and didymium. I find, however, that the ceric oxide produced by the first application of the process retains considerable quantities of lanthanum and didymium, and that these can only be separated by repeating the process several times. It is better, therefore, instead of leaving the liquid for a whole day in contact with the precipitate, to pour it off; fill up the vessel with fresh caustic potash; again pass chlorine through the liquid till it is saturated; and repeat this treatment till the yellow liquid, after being poured off from the precipitate and boiled till its colour disappears (whereupon a small quantity of ceric oxide separates from it, and must be removed by filtration), no longer gives a precipitate with caustic potash. When this point is attained, the ceric oxide is perfectly free from lanthanum and didymium. It still, however, retains considerable quantities of hypochlorous acid and salts of potash. The easiest mode of purifying it is to dissolve it in boiling hydrochloric acid (it dissolves with evolution of chlorine, and forms CeCl), and precipitate the cerium with oxalate of ammonia. The precipitated oxalate—which is easily washed, and is then free from all impurities—may be converted into ceric oxide by ignition; the ceric oxide converted into cerous sulphate by boiling with sulphuric and hydrochloric acid; and the protoxide precipitated by caustic potash. This mode of separation is troublesome, but effectual; it is useful also for detecting the presence of cerium when associated in small quantities with lanthanum and didymium. (W.)

(*c.*) The separation of cerium from lanthanum and didymium may, however, be much more easily effected by boiling the crude red-brown oxide, obtained by igniting the oxalate of the mixed oxides, in a solution of sal-ammoniac. The oxides of lanthanum and didymium then dissolve—being converted into chlorides, with evolution of ammonia—while pure ceric oxide remains behind. The boiling must be continued for several hours, and the solution poured off once or twice and fresh liquid added. The process must be continued till the decanted liquid no longer gives a precipitate with oxalate of ammonia. The ceric oxide is then of a light buff colour. It may be collected on a filter and washed with water containing sal-ammoniac: if pure water be used, the oxide immediately runs through the filter. The ammoniacal salt may then be driven off by ignition and the ceric oxide converted into cerous oxide as before. This mode of separation is the easiest and most effective of all. The solution of lanthanum and didymium is quite free from cerium (as I have proved by examining it by the chlorine process just described) and the ceric oxide is free from all traces of lanthanum and didymium. (W.) (*Vid. Qu. J. of Chem. Soc.* 2, 131.)

(*d.*) According to L. L. Buonaparte (*Comp. rend.* 16, 1008), cerium may be separated from didymium by means of valerianic acid. The hydrated oxides are precipitated by a caustic alkali; the cerous oxide converted into ceric oxide; the whole dissolved in nitric acid; the excess of acid driven off by a gentle heat; the residue mixed with a very small quantity of water; and a saturated solution of valerianic acid added, drop by drop, as long as any precipitate forms. This precipitate is valerianate of ceric oxide: valerianate of didymium remains in solution. The discoverer of this method has not stated whether oxide of lanthanum is precipitated or held in solution by the valerianic acid; but from its great similarity to didymium in its behaviour with other acids, we may presume that it would be held in solution. ¶

The mixture of lanthanum and didymium with cerium having been overlooked till within these last few years—all the statements here collected (even those of Mosander) respecting the compounds of cerium, relate to that which contains the allied metals. The only experiments made with pure cerium are those of Beringer, Rammelsberg, and Marignac. But considering the great similarity which exists between the three metals, it is probable that the descriptions here given will not be much altered by the investigation of pure cerium compounds. [The principal alterations relate to the properties of ceric oxide and the colour of the cerous salts. (W.)]

Hydrated protoxide of cerium is a white powder which rapidly turns yellow in the air from absorption of oxygen. (Berzelius.) Of the anhydrous protoxide little is known: it may be obtained by exposing the carbonate to a white heat in a current of hydrogen gas. (Berzelius.)

*b.* With acids, protoxide of cerium forms the PROTO-SALTS OF CERIUM, SALTS OF CEROUS OXIDE, or CEROUS SALTS. It is readily dissolved by acids. The insoluble salts of cerous oxide are white: those which are soluble form amethyst-coloured solutions with a small quantity of water, and colourless solutions with a larger quantity. The red colour arises neither from the presence of cobalt nor of manganese (Beringer); it is due to the presence of didymium. Pure cerous salts form perfectly colourless solutions. (Mosander.)

The soluble salts have a sweet, astringent taste, and redden litmus even when the acid is perfectly saturated. All cerous salts, the acids of which are volatile or easily decomposed, part with their acids on ignition, except the double sulphate of cerous oxide and potash. From solutions of cerous salts, ammonia and potash precipitate the hydrated protoxide in colourless, voluminous flakes, insoluble in an excess of the reagent. Alkaline sulphides act in a similar manner, with evolution of sulphuretted hydrogen. The normal carbonates and bicarbonates of ammonia and potash precipitate carbonate of cerous oxide in colourless flakes, slightly soluble in excess of the alkaline carbonate. Phosphate of soda throws down from the neutral salts a white precipitate of cerous phosphate, easily soluble in nitric acid. A saturated solution of sulphate of potash added to a solution of a cerous salt (not too dilute) produces—either at once or after some little time—a crystalline granular precipitate of double sulphate of cerous oxide and potash. Arseniate of potash gives a white precipitate. Oxalic acid and the alkaline oxalates—when the acid in combination with the cerium is not in too great excess—throw down colourless oxalate of cerous oxide, curdy at first, but afterwards changing to a fine, crystalline powder, which is soluble only in a large excess of hydrochloric or nitric acid. Tartrate of potash gives a precipitate readily soluble in acids. Succinate and benzoate of ammonia produce in a solution of not less than 1 part of salt in 100 parts of water, a white curdy precipitate. Ferrocyanide of potassium throws down colourless ferrocyanide of cerium, soluble in nitric acid. No change is produced by: hydrosulphuric acid, zinc, iron, carbonate of baryta, strontia or lime, ferricyanide of potassium, or tincture of galls.

### B. CEROSO-CERIC OXIDE.

Formed by igniting the sesquioxide in a current of hydrogen gas; also by strongly igniting the carbonate or oxalate of the protoxide in a *retort—under* which circumstances these acids impart a portion of oxygen

to the protoxide. Lemon-yellow powder, which, when heated in the air, burns and is converted into ceric oxide; it dissolves in hydrochloric acid with evolution of chlorine. (Berzelius.) Dilute acids separate the protoxide and leave the sesquioxide behind. (Beringer.)

Since 100 parts of ceric oxide, free from lanthanum, lose 1·176 parts of oxygen when reduced by hydrogen to the state of ceroso-ceric oxide, the latter oxide must be composed of $CeO + 4(Ce^2O^3)$. (Beringer.) According to Marignac, it is $3CeO + 2Ce^2O^3$. (*Arch. Ph. Nat.* 8, 266.)

*Hydrated ceroso-ceric oxide* is formed—mixed, according to Vauquelin, with carbonate of the protoxide—by exposing the hydrated protoxide to the air; it has a yellow colour. (Berzelius.)

### C. Sesquioxide of Cerium, or Ceric Oxide. $C^2O^3$.

*Formation.* The metal, when heated in the air, burns with a bright flame and abundant evolution of sparks, and is converted into the sesquioxide. (Mosander, Beringer.) The hydrated protoxide and the ceroso-ceric oxide are converted into sesquioxide by ignition in the air. The residue obtained by igniting the nitrate of cerous oxide also consists of ceric oxide. ¶ According to Marignac, the oxide thus obtained is the ceroso-ceric, composed of $3CeO + 2Ce2O^3$. Mosander likewise states that the oxide obtained by igniting the nitrate contains cerous oxide. (*Phil. Mag. J.* 28, 241.) ¶

*Properties.* Pure ceric oxide is a white, or very faintly coloured powder. ¶ Lemon-yellow: after an hour's ignition, it acquires a reddish tinge, but without the faintest trace of brown. (Mosander.) Fawn or salmon-coloured. (W.) ¶ Tasteless and infusible. (Mosander.) The ordinary oxide containing didymium is brownish-red, and, according to Karsten, has a specific gravity of about 5·6059.

Calculation, according to Hisinger.

| | | | |
|---|---|---|---|
| 2Ce | 92 | | 79·31 |
| 3O | 24 | | 20·69 |
| $Ce^2O^3$ | 116 | | 100·00 |

$Ce^2O^3 = 1149·4 + 300 = 1449·4$ (Berzelius.)

*Decomposition.* By ignition with hydrogen gas, ceric oxide is converted into ceroso-ceric oxide. (Berzelius.) When gently ignited in hydrogen gas, it becomes colourless, but the loss of weight is hardly appreciable. (Beringer.) When heated with hydrochloric acid, it evolves chlorine gas and is converted into hydrochlorate of the protoxide.

*Combinations.* *a.* With water. The hydrate is precipitated from solutions of ceric oxide salts by the fixed alkalis, as a pale-yellow viscid substance, which assumes a darker colour when dry. (Berzelius.) The hydrate free from didymium is of a sulphur-yellow colour. (Mosander.)

*b.* Ceric oxide is easily dissolved by acids, though in small quantity only.—When pure it is nearly insoluble in all acids, excepting hot oil of vitriol. (Mosander, Marignac, Watts.) Its salts are yellow or red in the solid state; their solutions are also of a yellow or reddish-yellow colour, and are characterized by a sour-sweet and very rough taste. When boiled with

hydrochloric acid they give off chlorine, and are converted into cerous salts. The fixed alkalis added to solutions of ceric salts, throw down pure hydrate of ceric oxide; ammonia generally precipitates a basic salt; and sulphate of potash, a yellow double salt.

## Cerium and Carbon.

Carbide of Cerium?—By strongly igniting protoxide of cerium moistened with oil in a porcelain retort, Laugier obtained a black shining substance, of the same weight as the protoxide employed, which inflamed spontaneously in the air, and was converted into brown ceric oxide. Oxalate of cerous oxide gently ignited in a porcelain retort, and then treated with an acid, leaves a brownish-black, insoluble powder, which when heated in the air, is rapidly converted into an equal weight of ceric oxide, the action being attended with incandescence. Hence it would appear to consist of $CeC^2$, inasmuch as $2CeC^2$ and $Ce^2O^3$ are of the same weight. A similar black powder is obtained by gently igniting the tartrate of cerous oxide. (Mosander.)

A. Carbonate of Cerous Oxide, or Cerous Carbonate.—Hydrated cerous oxide absorbs carbonic acid from the air and from water, and is thereby converted into a white granular powder. The precipitate produced in cerous salts on the addition of alkaline carbonates has a silvery lustre when dry, and is very light. (Vauquelin.) The precipitate formed by carbonate of ammonia appears at first in white, amorphous flakes; but these, in the course of three days, change beneath the liquid into shining crystalline scales, which unite on the filter to a silvery mass, easily separated from the paper. (Beringer.)

| | Calculation. | | Beringer. | Klaproth. | Hisinger. | Vauquelin. |
|---|---|---|---|---|---|---|
| CeO | 54 | 52·43 | 53·31 | 65 | 57·9 | 57 |
| $CO^2$ | 22 | 21·36 | 21·91 | 23 | 42·1 | 43 |
| 3HO | 27 | 26·21 | 24·78 | 12 | | |
| $CeO, CO^2 + 3Aq$ | 103 | 100·00 | 100·00 | 100 | 100·0 | 100 |

In a close vessel, the salt may be gently ignited without decomposition; but at a higher temperature it is converted into ceroso-ceric oxide, carbonic acid and carbonic oxide gases being at the same time evolved. If the air has access to it, the decomposition is more easily effected, and the residue consists of ceric oxide. (Hisinger & Berzelius.) The salt is insoluble in water and in aqueous carbonic acid. (Vauquelin.)

B. Carbonate of Ceric Oxide.—Formed by double decomposition. Of a dirty white colour. Easily soluble in water.

| | Calculation. | | Hisinger. |
|---|---|---|---|
| $Ce^2O^3$ | 116 | 63·74 | 63·83 |
| $3CO^2$ | 66 | 36·26 | 36·17 |
| $Ce^2O^3, 3CO^2$ | 182 | 100·00 | 100·00 |

### Cerium and Phosphorus.

A. Phosphide of Cerium.—Cerium heated with phosphorus to the boiling point of the latter, does not enter into combination with it. (Mosander.) When phosphuretted hydrogen gas is passed over ceric oxide heated to whiteness in a porcelain tube, and the contents allowed to cool out of contact of air, a grey powder is obtained, probably consisting of a mixture of phosphide of cerium and phosphate of cerous oxide. Heated in the air, it gradually turns white; it dissolves with difficulty even in the most concentrated acids, and without any escape of gas, as phosphate of cerous oxide. (Mosander.)

B. Phosphate of Cerous Oxide or Cerous Phosphate.—Formed by precipitating a soluble cerous salt with phosphoric acid or a phosphate. White powder, insoluble in water or in solution of phosphoric acid; slightly soluble in hydrochloric and nitric acids. (Hisinger & Berzelius.) By strong ignition in a charcoal crucible, it is neither fused nor reduced, but merely cakes together. (Mosander.)

Phosphate of cerium is found in an impure state in *Monazite* and *Edwardsite*, minerals which appear to be nearly identical; also in *Cryptolite* and *Phosphocerite*, which are likewise identical in all respects except crystalline form. *Monazite: Fig.* 85, the apex between $u'$, $u$ and $i$ being truncated; $i : u = 100°$; $u' : u = 95° 30'$; $i : a = 137° 30'$; $i$ = the face between $u'$, $u'$ and $i = 140° 30'$; $i : f = 125°$. (Brooke, *Phil. Mag. Ann.* 10, 189.)—Oblique rhombic prism, of specific gravity between 4·922 and 5·019. (Breithaupt.) Dissolves in hydrochloric acid with evolution of chlorine, leaving a white powder undissolved. Contains:

| | |
|---|---|
| Sesquioxide of cerium | 26·00 |
| Oxide of lanthanum | 23·40 |
| Protoxide of manganese | 1·86 |
| Binoxide of tin | 2·10 |
| Thorina | 17·95 |
| Lime | 1·68 |
| Phosphoric acid | 28·50 |
| Potash and binoxide of titanium (traces) | |
| | 101·49 |

(Kersten, *Pogg.* 47, 385.)

*Edwardsite:* Oblique rhombic prism; the base obliquely inclined to the acute lateral edge, the angle of which is 85°; this edge is truncated. Cleavage parallel to the base and to the longer diagonal; sp. gr. 4·2—4·6. Before the blowpipe it fuses at the edges to a clear glass. But slightly attacked by nitric acid. Contains:

| | |
|---|---|
| Protoxide of cerium | 56·53 |
| Alumina | 4·44 |
| Zirconia | 7·77 |
| Silica | 3·33 |
| Phosphoric acid | 26·66 |
| Magnesia, glucina, and protoxide of iron (traces) | |
| | 98·73 |

Shepard (*Sill. Am. J.* 32, 162; also *J. pr. Chem.* 12, 185); compare G. Rose (*Pogg.* 49, 223).

¶ *Cryptolite:* Discovered by Wöhler in the rose-coloured apatite of Arendal in Norway, from which it is separated by dissolving the apatite in nitric acid. The cryptolite is then left undissolved, together with microscopic crystals of magnetic iron-ore, hornblende, and an unknown substance of a hyacinth-red colour likewise containing cerium. The crystals of cryptolite are hexagonal prisms about a line in length, and of a wine-yellow colour. By exposure to a moderate heat, they undergo no change either in appearance or in weight. Sp. gr. = 4·6. Decomposed by strong sulphuric acid, the whole being reduced to a dry earthy mass.

| | |
|---|---|
| Sesquioxide of cerium | 73·70 |
| Protoxide of iron | 1·51 |
| Phosphoric acid | 27·37 |
| | 102·58 |

The excess arises from the protoxide of cerium contained in the mineral being converted by ignition into sesquioxide. (Wöhler, *Ann. Pharm.* 57, 268.)

*Phosphocerite:* Discovered by Mr. Ollive Sims in the cobalt-ore Johannisberg in Sweden, of which it forms about one-thousandth part. Remains as a residual product when the ore after calcination is treated with hydrochloric acid for the purpose of extracting the cobalt. Greyish-yellow crystalline powder, associated with a small quantity of minute dark purple crystals which are strongly attracted by the magnet, and appear to consist of magnetic iron-ore and oxide of cobalt.—The crystals of phosphocerite when examined by the microscope present two forms, one an octohedron (not regular), the other a four-sided prism with quadrilateral summits; both forms appear to belong to the right prismatic system. Hardness, between 5·0 and 5·5. (Chapman, *Qu. J. of Chem. Soc.* 2, 154.) Sp. gr. = 4·78. (W.) When exposed to the blowpipe flame, it vitrefies partially on the edges and surface, tinging the flame at the same time slightly green. With the usual blowpipe reagents, it presents the reactions of cerium, imparting however to the borax and phosphate of soda glasses, when cold, a pale violet-blue tint, either due to the presence of didymium or to the admixture of a small portion of the cobalt-ore. With borax and soft iron wire, it produces brittle phosphide of iron. (Chapman.) Oil of vitriol aided by gentle heat decomposes it, forming a pasty mass, which is soluble in cold water, with the exception of a small quantity of silica. Contains:

| | |
|---|---|
| Protoxide of cerium, &c. | 64·68 |
| Oxide of iron | 2·83 |
| Oxide of cobalt, silica, &c. | 3·41 |
| Phosphoric acid | 28·46 |
| | 99·38 |

The protoxide of cerium (including lanthanum and didymium) and phosphoric acid are very nearly in the proportions required to form a terbasic phosphate. Hence the mineral may be regarded as a mixture of the tribasic phosphates of cerium, lanthanum, and didymium. It is evidently identical in composition with cryptolite; but the crystalline forms of the two minerals (as far at least as they can be ascertained) are totally incompatible. Probably, therefore, the phosphate of cerous oxide is dimorphous. (W.) ¶

### Cerium and Sulphur.

A. Protosulphide of Cerium.—1. Cerium heated in vapour of sulphur absorbs it and becomes red hot.—2. Vapour of bisulphide of carbon passed over ignited cerous carbonate (or over ceric oxide, *Beringer*), converts it into sulphide of cerium, of loose texture and the colour of red-lead.—3. When a mixture of 1 part of ceric oxide and 3 parts of liver of sulphur is strongly ignited in a covered vessel for half an hour, and the sulphide of potassium dissolved out by water,—sulphide of cerium remains, in small crystalline scales, resembling mosaic gold, greasy to the touch, sometimes of a yellowish green, sometimes of a golden yellow colour: when examined by a lens, they appear translucent, with a yellow tint. When sulphide of cerium is heated in a gas which does not decompose it, its yellow colour changes, through red, to dark red and black, but is again restored on cooling. It does not appear to conduct electricity.—If instead of ceric oxide, hydrated chloride of cerium (CeCl, HO) is ignited with the liver of sulphur, the sulphide of cerium remains, after washing the residue, in the form of a scaly powder, which appears dirty yellow while diffused in water, but assumes a dirty red colour, after settling to the bottom of the vessel, or after drying.

| | Calculation. | | Mosander. |
|---|---|---|---|
| Ce ..... | 46 .... | 74·19 .... | 74 |
| S ..... | 16 .... | 25·81 .... | 26 |
| CeS ..... | 62 .... | 100·00 .... | 100 |

Sulphide of cerium remains unaltered in air and water. Heated in the air, it takes fire below a red heat and burns with a blue flame and evolution of sulphurous acid: the product is basic sulphate of ceric oxide. Heated in a current of chlorine gas, it is resolved into chloride of cerium and chloride of sulphur. It is not altered by ignition in vapour of iodine or of potassium, or when heated with phosphorus. It is dissolved by the weakest acids, forming a cerous salt and evolving sulphuretted hydrogen gas without separation of sulphur. Only the sulphide prepared by the third method deposits 1 or 2 per cent. of sulphur, when dissolved in acids: this sulphur, however, is present merely in the state of mechanical mixture, in consequence of a portion of the liver of sulphur having been decomposed by the air contained in the water, and may be expelled by heating the sulphide of cerium in an atmosphere of hydrogen gas. In solution of potash, sulphide of cerium is changed into a green powder, which appears to consist of oxysulphide of cerium. (Mosander.)

B. Sesquisulphide of Cerium.—Not yet isolated, but known only in combination with electro-negative metallic sulphides.

C. Oxysulphide of Cerium.—Carbonate of cerous oxide is distilled with sulphur or ignited in a current of sulphuretted hydrogen gas.—Apple-green powder. Dissolved by acids with evolution of sulphuretted hydrogen and separation of sulphur. Generally contains a small quantity of basic sulphate of cerous oxide. (Berzelius.)

D. Sulphite of Cerous Oxide or Cerous Sulphite.—Prepared by dissolving carbonate of cerous oxide in an aqueous solution of sulphurous acid. Crystallizes in pale amethyst-coloured needles. (Klaproth.)

E. Hyposulphate of Cerous Oxide or Cerous Hyposulphate.—Carbonate of cerous oxide is dissolved in aqueous hyposulphuric acid and the solution left to evaporate in the air spontaneously. Slender, colourless, four-sided prisms, permanent in the air, and containing after abstraction of water, 42·79 per cent. of base and 57·21 of acid. (Heeren.)

F. Sulphate of Cerous Oxide or Cerous Sulphate.—*a. Basic Sulphate.*—1. Remains after ignition of salt *b* in close vessels.—2. Precipitated from a solution of salt *b*, by excess of ammonia. Even potash does not separate the whole of the sulphuric acid. (Hisinger & Berzelius.)

*b. Monosulphate:* Prepared by dissolving carbonate of cerous oxide in cold dilute sulphuric acid—or, according to Berthier, by treating ceric oxide with aqueous solution of sulphurous acid, evaporating to the crystallizing point, and dehydrating the crystals which are formed. The anhydrous salt is a white powder, of a sweetish-astringent and slightly acid taste. Heated in a close vessel, it leaves basic sulphate of cerous oxide; but if heated in an open vessel, it leaves basic sulphate of ceric oxide. (Hisinger & Berzelius.)

| | Anhydrous. | | Rammelsberg. | Beringer. |
|---|---|---|---|---|
| CeO ..... | 54 .... | 57·45 .... | 57·306 .... | 57·442 |
| $SO^3$ ..... | 40 .... | 42·55 .... | 42·694 .... | 42·558 |
| CeO, $SO^3$ .... | 94 .... | 100·00 .... | 100·000 .... | 100·000 |

*Combinations with water.*—The anhydrous salt sprinkled with a small quantity of water evolves considerable heat and condenses to a solid mass, which dissolves with difficulty. (Otto.)

*α. With* $1\frac{1}{2}$ *atoms of water.*—On boiling a solution of this salt in cold water, the salt *α* is deposited in small pale-red crystals, which are again dissolved as the liquid cools. By pouring off the boiling liquid, the crystals may be obtained separate. (Otto, *Pogg.* 40, 404.)

*β. With* 3 *atoms of water.*—Crystallizes out on the slow evaporation of an aqueous solution. Pale amethyst-coloured prisms (Hisinger & Berzelius, Klaproth); colourless crystals (Vauquelin). Right rhombic prisms having two of their lateral edges truncated, and with dihedral summits the faces of which rest upon the other two lateral edges. (Marx, *Schw.* 52, 481.) ¶ Rhombic octohedrons, the faces of which meet in the terminal edges at angles of 114° 12′ and 111° 10′: frequently also in more acute octohedrons, the corresponding angles of which are 99° 48′ and 95° 48′. (Marignac, *Ann. Pharm.* 68, 214.) ¶

Sulphate of cerous oxide is dissolved with difficulty by water, producing a pale reddish solution. [Colourless when free from didymium.]

| | Sesqui-hydrated. | | Otto. |
|---|---|---|---|
| 2CeO ..... | 108 .... | 50·23 | |
| $2SO^3$ ..... | 80 .... | 37·21 .... | 36·94 |
| 3HO ..... | 27 .... | 12·56 .... | 12·58 |
| 2(CeO, $SO^3$) + 3Aq. | 215 .... | 100·00 | |

| | Ter-hydrated. | | Otto. |
|---|---|---|---|
| CeO ..... | 54 .... | 44·63 | |
| $SO^3$ ..... | 40 .... | 33·06 | |
| 3HO ..... | 27 .... | 22·31 .... | 22·5 |
| CeO, $SO^3$ + 3Aq. .... | 121 .... | 100·00 | |

¶ G. CEROSO-CERIC SULPHATE.—Analysed by Marignac. (Marignac, *Arch. des Sc. phys. & nat.* 8, 278.)

| | Calculation. | | Marignac. |
|---|---|---|---|
| $3CeO$ | 162 .... | 26·49 | |
| $2Ce^2O^3$ | 232 .... | 37·87 .... | 37·05 |
| $4SO^3$ | 160 .... | 25·57 .... | 26·09 |
| $7HO$ | 63 .... | 10·07 .... | 10·10 |
| $3CeO, 2Ce^2O^3, 4SO^3 + 7Aq.$ .... | 617 .... | 100·00 | ¶ |

H. SULPHATE OF CERIC OXIDE, or CERIC SULPHATE.—*a. Polybasic sulphate.*—Formed by digesting *b* with ammonia. Light flesh-coloured powder. (Berzelius.)

*b. Basic sulphate.*—1. Prepared by igniting the salt *c*. (Berzelius.)—2. By burning sulphide of cerium. (Mosander.) Dark brick-red powder. Not decomposed by strong ignition. Soluble in hydrochloric acid, forming a reddish-yellow solution, from which it is precipitated by alkalis unchanged.

*c. Tersulphate.*—$Ce^2O^3, 3SO^3$.—The lemon-coloured solution of ceric oxide in dilute sulphuric acid yields, by slow evaporation, lemon-coloured prisms, which, when exposed to the air, gradually effloresce and lose their colour. (Hisinger & Berzelius.)

Hydro-sulphocarbonate of lime does not precipitate a solution of protochloride of cerium; the liquid remains clear for several hours and then deposits white flakes. (Berzelius.)

## CERIUM AND SELENIUM.

A. SELENIDE OF CERIUM.—Selenite of cerous oxide heated to redness in a porcelain tube is decomposed by a current of hydrogen gas. If ceric oxide is present, a portion of selenium passes off with the hydrogen. Brownish powder, constantly evolving an unpleasant odour of seleniuretted hydrogen. When heated in the air, it yields a sublimate of selenious acid, and leaves a white powder, which dissolves with great difficulty in acids, and probably consists of basic selenite of ceric oxide. Selenide of cerium dissolves in the weakest acids with evolution of seleniuretted hydrogen. Water has no action on it. (Berzelius.)

Aqueous solutions of cerous salts give with alkaline hydroseleniates a pale red precipitate, which becomes darker in the air from decomposition. (Berzelius.) Probably *hydrated selenide of cerium*, or *hydroseleniate of cerous oxide.*

B. SELENITE OF CEROUS OXIDE, or CEROUS SELENITE.—*a. Monoselenite.*—White powder, insoluble in water.

*b. Bi-selenite.*—The *normal-salt* dissolves in an aqueous solution of selenious acid. (Berzelius.)

C. SELENITE OF CERIC OXIDE, or CERIC SELENITE.—*a.* Lemon-coloured powder, which parts with its acid when ignited.

*b. Bi-selenite.*—Formed by dissolving the salt *a* in aqueous selenious acid. The solution dries up on evaporation to a yellow varnish, which loses water when heated, and becomes white, opaque, and crystalline. Soluble in water. (Berzelius.)

## Cerium and Iodine.

Iodide of Cerium.—A solution of protoxide of cerium in aqueous hydriodic acid becomes coloured on evaporation, from separation of iodine, and leaves ceric oxide after ignition. (Beringer.)

## Cerium and Bromine.

A. Bromide of Cerium, and Hydrobromate of Cerous Oxide.—The colourless solution of ceric oxide in aqueous hydrobromic acid yields small crystals on evaporation; and if the evaporation be continued, it evolves hydrobromic acid, and leaves a solid, highly deliquescent residue, which, when heated, becomes tenacious and then solidifies again. When this residue is strongly ignited, the bromine is partially expelled, and an insoluble *oxybromide of cerium* remains, which, on the addition of nitric acid, evolves bromine. (Berthemot, *Ann. Chim. Phys.* 44, 393.)

B. Bromate of Cerous Oxide, or Cerous Bromate.—A hot saturated solution of cerous sulphate is precipitated by an equivalent quantity of bromate of baryta, and the filtrate concentrated under the evaporating receiver over oil of vitriol. Colourless, laminated, and fibrous crystals, with yellow spots here and there: they do not effloresce, even when kept for a lengthened period under the receiver, and leave ceric oxide after ignition. Readily soluble in water. (Rammelsberg, *Pogg.* 55, 63.)

| | Crystallized. | | Rammelsberg. |
|---|---|---|---|
| CeO ..... | 54·0 .... | 23·85 .... | 24·08 |
| $BrO^5$ ..... | 118·4 .... | 52·30 | |
| 6HO ..... | 54·0 .... | 23·85 | |
| $CeO, BrO^5 + 6Aq.$ ..... | 226·4 .... | 100·00 | |

## Cerium and Chlorine.

A. Chloride of Cerium.—Cerium burns vividly when heated in chlorine gas. (Mosander.) Chlorine passed over ignited ceric oxide, forms chloride of cerium, mixed however with oxide; a small quantity of white oxychloride is also sublimed. (Beringer.) *Preparation.*—1. Heated sulphide of cerium is decomposed by dry chlorine gas. (III., 267.) If all the atmospheric air is not expelled by the chlorine before the sulphide is heated, an infusible mixture is obtained, consisting of chloride and protoxide of cerium. (Mosander.)—2. A solution of protoxide of cerium in hydrochloric acid is evaporated to dryness, after the addition of sal-ammoniac; and the ammoniacal salt, together with the last trace of water, expelled by exposure to a strong heat: it is best to heat the substance in a glass tube through which a rapid current of dry chlorine is made to pass. (Beringer.)

White, porous, fusible at a red heat. (Mosander.) Semifused mass. (Beringer.) Potassium and sodium decompose it with the aid of heat (Mosander), but without producing perceptible ignition. (Beringer.) Perfectly soluble in water.

| | Calculation. | | Beringer. | Or: | | | Hisinger. |
|---|---|---|---|---|---|---|---|
| Ce ..... | 46·0 | 56·51 | 56·55 | CeO ..... | 54·0 | 66·34 | 66·376 |
| Cl ..... | 35·4 | 43·49 | 43·45 | $MuO^2$..... | 27·4 | 33·66 | 33·624 |
| CeCl ..... | 81·4 | 100·00 | 100·00 | | 81·4 | 100·00 | 100·000 |

*Hydrated Protochloride of Cerium*, or *Cerous Hydrochlorate*.—Formed by dissolving the hydrate or carbonate of cerous or ceric oxide, in boiling hydrochloric acid, and evaporating to a syrupy consistence. Pale rose-coloured crystals (Vauquelin, Beringer); colourless, four-sided prisms (Hisinger & Berzelius). The crystals heated in a retort give off, first water and then hydrochloric acid (if hydrochlorate of ceric oxide is present, chlorine is likewise evolved), leaving a compound of protochloride and sesquichloride of cerium, or ceroso-ceric chloride. (Berzelius.)

Both the anhydrous and the hydrated chloride of cerium deliquesce in the air. The aqueous solution is colourless, but soon turns yellow on exposure to the air, from formation of a ceric salt. A solution of the salt in alcohol burns with a green, scintillating flame. (Berzelius.)

B. Oxychloride of Cerium.—1. Remains in the retort after heating the hydrated chloride of cerium. (Berzelius.)—2. Formed during the decomposition of sulphide of cerium by chlorine, if the air be not completely excluded. (Mosander.) White; turns yellow when moistened and exposed to the air. Insoluble in acids. Decomposed by fusion with alkalis. (Berzelius.) Leaves pure ceric oxide when strongly ignited in an open vessel. (Beringer.)

C. Hydrated Sesquichloride of Cerium, or Ceric Hydrochlorate.—The reddish-yellow solution of ceric oxide in cold hydrochloric acid—the acid being in excess—evolves chlorine gas on the slightest elevation of temperature, and assumes a golden-yellow colour; it is afterwards found to contain a mixture of protochloride and sesquichloride of cerium (or hydrochlorate of ceroso-ceric oxide): after prolonged ebullition, protochloride of cerium alone remains. (Berzelius.)

## Cerium and Fluorine.

A. Protofluoride of Cerium.—Formed by precipitating protochloride of cerium with an alkaline fluoride. White, insoluble in water. (Berzelius.) It is only partially reduced by exposure in a heated state to a mixture of hydrogen gas and vapour of potassium. (Mosander.)

B. Sesquifluoride of Cerium.—Prepared in a similar manner. Yellow, and insoluble in water. Occurs in six-sided prisms, mixed with half its weight of protofluoride of cerium; also with fluoride of yttrium and fluoride of calcium, as *Yttrocerite*.

*Hydrated Sesquifluoride with Sesquioxide of Cerium*, or *Sesqui-hydrofluate of Ceric oxide* ($Ce^2F^3, Ce^2O^3 + 3Aq = 2CeO^2O^3, 3HF$), occurs as *Basic Fluoride of Cerium*.

## Cerium and Nitrogen.

A. Nitrate of Cerous Oxide, or Cerous Nitrate.—The solution evaporated to the consistence of syrup, yields colourless, tabular crystals.

(Berzelius.) Beringer did not obtain any crystals; Vauquelin, only from an acid solution. When ignited, it leaves ceric oxide. Dissolves readily in water and in 2 parts of alcohol. (Vauquelin.)

B. Nitrate of Ceric Oxide, or Ceric Nitrate.—The oxide dissolves in nitric acid, slowly and with difficulty, giving rise to a reddish-yellow solution, which becomes colourless when diluted. (Klaproth.) By evaporation, a reddish-yellow crystalline mass is obtained, resembling honey in appearance, and absorbing moisture from the air. (Berzelius.)

C. Carbonate of Cerous Oxide and Ammonia.—Carbonate of cerous oxide is slightly soluble in an aqueous solution of carbonate of ammonia. (Berzelius.)

D. Sulphate of Cerous Oxide and Ammonia.—The solutions of the two salts do not become turbid immediately on being mixed; but in the course of 24 hours, small crystals are deposited. The double salt is also separated in the form of a crystalline powder, by boiling the mixed solutions; it may be purified by re-solution in water and crystallization. Pale, rose-coloured, obtuse rhombohedrons, soluble in water. (Beringer.)

## Cerium and Potassium.

The oxides of cerium do not combine with potash, either in the wet or in the dry way.

A. Carbonate of Cerous Oxide and Potash.—Cerous oxide may be fused with carbonate of potash: the compound dissolves in water, forming a yellow solution. A similar liquid is obtained by dissolving the hydrate or carbonate of cerous oxide in an aqueous solution of carbonate of potash. Acids precipitate the cerous oxide. (Hisinger & Berzelius.)

B. Carbonate of Ceric Oxide and Potash.—Carbonate of potash dissolves a small quantity of hydrated ceric oxide. (Berzelius.)

C. Sulphate of Cerous Oxide and Potash.—Precipitated on mixing the solution of a cerous salt with sulphuric acid and potash: *e. g.*, a concentrated solution of a cerous salt with a solution of sulphate of potash or with crystals of sulphate of potash. The precipitation is not prevented by excess of acid, but does not take place if the solution is too dilute. According to Th. Scheerer, any sesquioxide of iron which may be present in the liquid, is carried down with the double salt, and gives it a yellow colour. The double sulphate is also precipitated, when a mass of crystallized sulphate of potash is suspended in the solution of a cerous salt; and by arranging the crystals of sulphate of potash so that they may reach to the surface of the liquid, the whole of the cerium may be separated in combination with the potash. The double salt is precipitated in the form of a white powder, which, after being purified with cold water and dissolved in boiling water, is deposited in small, colourless crystals. (Berzelius.) The double salt, when precipitated by suspending a mass of crystallized sulphate of potash in a cerium solution, contains a slight excess of sulphate of potash, which is not entirely separated by

washing and recrystallization. (Beringer.) It fuses at a red heat without decomposition. (Berzelius.) If the double salt is fused with three times its weight of carbonate of soda, and the mass exhausted with water, ceric oxide remains, free from sulphuric acid, but not easily soluble in boiling hydrochloric acid. (Beringer.) From a hot aqueous solution of this salt, caustic potash or carbonate of potash precipitates hydrated cerous oxide mixed with basic cerous sulphate, unless the mixture is digested or boiled for a considerable time; in that case, all the sulphuric acid is separated. Sulphuric and other acids dissolve the double salt, at the same time converting the normal sulphate of potash into bisulphate. Boiling water dissolves the double salt rather freely; cold water but slightly; and water saturated with sulphate of potash, not at all. (Berzelius.)

D. Sulphate of Ceric Oxide and Potash. — Precipitated by mixing ceric sulphate with a small quantity of potash or sulphate of potash; it has an orange-yellow colour, and is difficultly soluble in water. (Hisinger & Berzelius.) Separates from a hot aqueous solution in dark yellow crystals. From a solution of this salt, potash throws down pure ceric oxide; ammonia, however, and carbonate of ammonia or potash, precipitate ceric oxide mixed with sulphuric acid. (Berzelius.) The double salt is thrown down as a sulphur-yellow precipitate from a solution of ceric oxide in nitric acid, on the addition of sulphate of potash; if, however, the nitric acid solution be previously boiled or mixed with hydrochloric acid, sulphate of potash produces a white precipitate. (Th. Scheerer, *Pogg.* 56, 499.)

## Cerium and Sodium.

The oxides of cerium do not combine with pure soda.

A. and B. The protoxide and sesquioxide of cerium form, with a solution of carbonate of soda, a compound similar to that which they form with carbonate of potash.—The oxides do not unite with carbonate of soda before the blowpipe.

C. and D. Borax or phosphate of soda and ammonia yields with ceric oxide, a clear glass, which is deep red while hot, but becomes colourless on cooling; when heated in the inner flame of the blowpipe with an excess of ceric oxide, it forms a yellow enamel. (Berzelius.)

E. Sulphate of Cerous Oxide and Soda.—From a solution of cerous sulphate, a saturated solution of Glauber's salt precipitates the double salt, rendering the liquid turbid; by heating the mixture to the boiling point, the cerium is completely precipitated. Or, if crystallized Glauber's salt is suspended in a solution of cerous sulphate, nearly all the cerium is separated in the form of the double sulphate. (Beringer.)

| | Calculation. | | Beringer. |
|---|---|---|---|
| NaO ..... | 31·2 | 12·04 | 12·694 |
| 2CeO ..... | 108·0 | 41·67 | 41·248 |
| $3SO^3$ ..... | 120·0 | 46·29 | 46·058 |
| $NaO,SO^3 + 2(CeO,SO^3)$ | 259·2 | 100·00 | 100·000 |

¶ Cerium and Calcium.

Carbonate of Cerous Oxide and Lime.—Occurs native in *Parisite*, a new cerium mineral discovered in New Granada, by L. Spada. Belongs to the rhombohedral system of crystallization. It forms bipyramidal dodecahedrons, the angles at the lateral edges being 120° 34′, and at the edges of the base 164° 58′; hence the ratio of the axes = 1 : 0·1524. Hardness, between felspar and apatite; specific gravity = 4·35. Colour greenish-yellow, with a tinge of red, like that which occurs in many zinc ores. Fracture yellowish-white, of a glassy lustre and slightly conchoidal. Transparent in thin laminæ; thicker pieces appear highly translucent at the edges. When heated in a glass tube, it evolves water and carbonic acid, acquires a cinnamon colour and becomes very friable. Before the blowpipe, it is infusible and incandescent; with borax it forms a yellow bead, which becomes colourless on cooling. Difficultly soluble in hydrochloric acid, producing effervescence. Contains in 100 parts: cerium, &c. 50·78, calcium 8·29, fluorine 5·49, oxygen 9·55, carbonic acid 23·50, water 3·38 = 8 (CeO, LaO, DiO; CaO) $CO^2$ + (CeO, LaO, DiO) HO + 2Ca F. (Bunsen, *Ann. Pharm.* 53, 147.) ¶

Cerium likewise combines with iron.

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Chapter IX.

# LANTHANUM.

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Mosander, *Pogg.* 46, 648; 47, 207; 56, 504.
Watts, *Qu. J. of Chem. Soc. London*, 2, 131.

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*History.* Mosander discovered, in 1839, that the oxide of cerium, as then prepared, contained (besides oxide of didymium) another metallic oxide, which, on account of its having so long escaped notice, he named Lanthanum (from λανθάνειν, *to lie hid*).

*Sources.* This metal appears to be invariably associated with cerium. It is accordingly found as oxide of lanthanum in Cerite, Euxenite, Monazite, the Gadolinite of Ytterby, Tschewkinite, Mosandrite, &c.

*Preparation.* A solution of oxide of lanthanum in hydrochloric acid is evaporated to dryness; the residue heated in a current of hydrochloric acid gas, to render it perfectly anhydrous; and the chloride of lanthanum decomposed by sodium with the aid of heat. The resulting chloride of sodium is then dissolved out by alcohol of specific gravity 0·833; the small quantity of oxide of lanthanum produced, washed away from the metal; the finely-divided lanthanum dried by pressure between folds of blotting-paper, and finally in vacuo over oil of vitriol. (Mosander.)

*Properties.* Dark lead-grey metallic powder, soft to the touch, and adhering by pressure. (Mosander.)

*Atomic weight:* 44·3 (Rammelsberg); 36·15 (Choubine); 36·1 (Otto); below that of cerium. (Mosander.)

## *Compounds of Lanthanum.*

### Lanthanum and Oxygen.

### A. Oxide of Lanthanum. LaO.

*Formation.* Lanthanum is slowly oxidized by exposure to the air. It evolves hydrogen gas slowly in cold water, rapidly in hot water, and is converted into a viscid hydrate of the oxide. (Mosander.)

*Preparation.* The hydrated cerous or ceric oxide containing lanthanum, and prepared from cerite by either of the methods 1—10 (pp. 259—261) is dissolved in nitric acid, evaporated to dryness, and ignited until all the nitric acid is expelled. The powdered residue is then digested for some hours at a gentle heat with a mixture of one part of nitric acid and from 50 to 100 parts of water; the nitrate of lanthanum filtered from the ceric oxide, which is nearly insoluble in the dilute acid; and carbonate of lanthanum precipitated from the filtrate by carbonate of ammonia. The precipitate, in the course of twenty-four hours, collects into shining scales, easily washed on the filter; and from these, by drying and prolonged ignition, oxide of lanthanum is obtained. (Mosander.)—A small quantity of ceric oxide is invariably present in the nitric acid solution, the presence of the lanthanum seeming to increase its solubility. (Mosander.) The presence of a basic salt, or of an alkali, also favours its solution. On this account, the oxide of lanthanum prepared as above must be dissolved in hydrochloric acid—the solution neutralized as exactly as possible with ammonia—acetate of ammonia added—and lastly oxalate of ammonia. The precipitate thus formed is to be collected on a double filter (*vid.* p. 259, note); the turbid liquid which first runs through poured back; the oxalate washed, dried, and ignited; and the remaining oxide once more dissolved in nitric acid, which still leaves behind a small quantity of ceric oxide. (H. Scheerer, *Pogg.* 56, 498.)

¶ The solution obtained by this process contains didymium as well as lanthanum. It has already been observed that the oxide of lanthanum dissolves in dilute acids more readily than the oxide of didymium: hence if the dilute nitric acid be poured off from time to time, and fresh acid added, the first solutions will be richer in lanthanum, the last in didymium; and *if the first portion of* acid be poured off after it has acted on

the red-brown oxide for a few minutes, and especially if it be kept quite cool, the solution obtained contains but a very small quantity of didymium. This is a very good way of obtaining a solution of lanthanum *nearly* pure.

The complete separation of lanthanum and didymium is one of the most difficult problems in chemistry: indeed, there is no method known by which this separation can be at once effected: it can only be accomplished by repeated crystallization of the sulphates.—1. The sulphates of lanthanum and didymium, when in the anhydrous state, dissolve with ease in a very small quantity of water at temperatures below 9° C. or 48° Fah.; and when the solution is gently heated, the sulphate of lanthanum crystallizes out first.—A solution of lanthanum and didymium free from cerium having been obtained by either of the methods already described (pp. 259—261), the mixed oxides are precipitated by caustic potash, and the precipitate, after washing, dissolved in dilute sulphuric acid. The solution is then evaporated to dryness, and the residue gently heated in a platinum capsule to drive off the excess of acid, and render the mixed sulphates anhydrous. The anhydrous sulphates are then dissolved in rather less than six times their weight of water at a temperature of 2° or 3° (36° or 37° F.), the salt being reduced to powder and added in small portions at a time, and the vessel containing the liquid surrounded with ice-cold water. If these precautions were not taken, the temperature of the liquid might rise above 9°, and then crystallization would commence and rapidly extend throughout the whole mass of liquid: but if the water be properly cooled, the sulphates dissolve completely. A solution having been thus obtained, it is to be gradually heated by a water-bath to rather more than 40° (104° F.). The sulphate of lanthanum then crystallizes out, accompanied by only a small quantity of the didymium salt. To purify it completely, it must be again rendered anhydrous, redissolved in ice-cold water, &c., the whole process being repeated ten or twelve times before the sulphate of lanthanum is obtained quite pure. The test of purity is perfect whiteness: the smallest quantity of didymium imparts an amethyst tinge. (Mosander.)—2. When an acid solution of the mixed sulphates of lanthanum and didymium is left to spontaneous evaporation in a warm place, the sulphate of didymium crystallizes out first; and if the didymium is in excess, two sorts of crystals collect at the bottom of the vessel. (*a*.) Large rose-coloured rhombohedral crystals modified with numerous secondary faces. (*b*.) Slender, prismatic, violet-coloured crystals, which adhere to the sides of the basin: the former are nearly pure sulphate of didymium; the latter consist of the two sulphates mixed. (Mosander.)—Further, if the rose-coloured crystals be removed; the violet-crystals redissolved; the solution mixed with the mother-liquid; and the whole again subjected to slow evaporation—no more large crystals of didymium-salt are obtained, but the solution yields small rhombohedral crystals of a violet colour; and by taking these out—evaporating the liquid still further—and repeating these operations three or four times, the solution at length becomes perfectly colourless—and when evaporated to dryness, yields a colourless residue of sulphate of lanthanum. The solution in this state yields perfectly colourless precipitates with alkalis, alkaline carbonates, and oxalate of ammonia. (W.) ¶

*Properties.* White powder. If contaminated with oxide of didymium it appears of a brick-red colour after ignition, but becomes greenish-white

after being heated to redness in hydrogen gas. In the red state it is more easily dissolved by acids, and yields a solution and crystals of a reddish colour; in the greenish-white state, it yields greenish solutions and crystals. ¶ When perfectly white carbonate of lanthanum in small lumps is strongly ignited in an open vessel, the surface of the lumps turns brown, while the inner portions remain white; on breaking up the lumps, and stirring, to renew the surface of contact with the air, the whole becomes light brown; but it is difficult to obtain it of a uniform colour. In a platinum crucible with a closely fitting cover, carbonate of lanthanum undergoes no change of appearance, even at a bright red heat. Hence it would appear that the brown colour just spoken of is due to the formation of a higher oxide, rather than to the presence of didymium. Carbonate of didymium, when ignited, becomes dark brown in a very short time. If perfectly white carbonate of lanthanum is dissolved in nitric acid, the solution evaporated to dryness, and the residue ignited, an oxide is obtained of a uniform brown colour. These facts seem to indicate that the brown colour is essential to the anhydrous oxide of lanthanum, and does not arise from the presence of didymium. The brown substance may, however, as already suggested, be an oxide of higher degree of oxidation than the protoxide. (W.) ¶ Oxide of lanthanum is not decomposed by potassium. (Mosander.)

*Combinations.* *a.* With water.—Hydrated Oxide of Lanthanum. —The metal or its oxide, when immersed in warm water, is gradually converted into the hydrate. Potash precipitates this hydrate from the salts of lanthanum. White; turns reddened litmus-paper slightly blue. The recently prepared hydrate is viscid while moist. That which is thrown down by potash stops up the pores of a filter. (Mosander.) ¶ Absorbs carbonic acid from the air with great rapidity, so that when washed on a filter, it is generally converted into carbonate, before the washing is completed. (Mosander.) ¶

*b.* With acids.—Salts of Lanthanum.—The oxide, even after strong ignition, dissolves easily in acids. When boiled in solution of sal-ammoniac, it dissolves and drives out the ammonia. The salts are colourless, when free from didymium. Those which are soluble have an astringent taste, with a scarcely perceptible trace of sweetness. Potash precipitates the hydrate from them in a very viscid state. (Mosander.) So likewise do caustic ammonia and hydrosulphate of ammonia. The precipitate is not soluble in excess of the alkali. ¶ According to Mosander, ammonia precipitates from the solutions of lanthanum, basic salts which are very viscid and dissolve in pure water, forming a milky solution which passes through the filter. If the basic salt is left for some time on a filter, it absorbs carbonic acid, and a neutral salt is formed, which dissolves and filters through, leaving carbonate of lanthanum behind. ¶ The normal carbonate or bicarbonate of ammonia or potash gives a white precipitate insoluble in excess of the alkaline carbonate; phosphate of soda white; alkaline oxalates, a white powder, not dissolved by water or saline solutions. (Choubine, *J. pr. Chem.* 26, 443.) Sulphate of potash does not affect a solution of lanthanum; a precipitate would indicate the presence of cerium. (Mosander.)

### B. Peroxide of Lanthanum.

Obtained only as *hydrate* by precipitating a neutral salt of lanthanum with peroxide of barium. White, with a yellowish tint (probably arising from didymium). Loses oxygen as it becomes dry. [Possibly the brown substance obtained by igniting the carbonate or nitrate, may be this oxide in the anhydrous state. (W.)]

## Lanthanum and Carbon.

Carbonate of Lanthanum.—Found native in small crystalline scales containing traces of protoxide of cerium (Mosander); formerly regarded as carbonate of the protoxide of cerium. The precipitate produced in solutions of lanthanum by alkaline carbonates is gradually converted into shining, crystalline scales, which, after being thoroughly washed and dried, form a shining coherent mass. (Mosander.) By precipitating a hot solution, crystalline scales are obtained; but in the cold, a horny translucent mass is formed resembling hydrate of alumina. (Bolley.) The complete expulsion of the carbonic acid can only be effected by long continued ignition. (Mosander.) (*Vid.* p. 277.)

## Lanthanum and Phosphorus.

Phosphate of Lanthanum.—The white precipitate which ordinary diphosphate of soda produces in lanthanum solutions is soluble in acids. (Choubine.)

## Lanthanum and Sulphur.

A. Sulphide of Lanthanum.—Lanthanum ignited in an atmosphere of bisulphide of carbon, forms a yellow mass, which is converted by cold water into hydrated oxide of lanthanum and free hydrosulphuric acid. (Mosander.) If 1 part of oxide of lanthanum is ignited with 3 parts of soda liver of sulphur, and the product exhausted with water, a reddish-yellow residue remains, which, when examined by the microscope, is found to consist of translucent crystals. (Beringer, *Ann. Pharm.* 42, 139.)

B. Sulphate of Lanthanum.—The salt, when dehydrated by ignition, has a reddish-white tint, and contains 56·642 per cent. of oxide of lanthanum, and 43·358 of acid. The hydrated crystals are of an amethyst red colour. (Rammelsberg, *Pogg.* 55, 65.) [The reddish hue is caused by didymium.] The crystals belong to the right prismatic system. Right rhombic prisms, having their acute lateral edges and their acute summits truncated; therefore, with $u$, $t$, and $i$-faces; $u^1 : u = 96° 36'$. (Bolley, *Ann. Pharm.* 33, 126.) ¶ Crystallizes in small six-sided prisms, with hexagonal summits, containing 3 atoms of water. It is much less soluble in warm than in cold water; at 2° or 3° it dissolves in 6 parts of water; at 23°, in 42½ parts; and at 100° it requires 115 parts for solution. (*Vid.* p. 276.) At a strong red heat, it loses half its acid, and is converted into an insoluble basic salt. (Mosander.) ¶

### Lanthanum and Bromine.

Bromate of Lanthanum.—Bromate of baryta is precipitated by an equivalent quantity of sulphate of lanthanum, and the filtrate concentrated under the evaporating receiver, over oil of vitriol. The pale amethyst-coloured crystals contain 23·67 per cent. of oxide of lanthanum. At 100° they lose 18·08 per cent. of water; at 160° (320° F.) altogether, 20·38 per cent. At a somewhat higher temperature, they rapidly evolve vapour of bromine and oxygen gas, and leave a white bulky residue consisting of a mixture of bromide and oxide of lanthanum, in which the bromine amounts to 29·36 per cent. (Rammelsberg.) The crystals exactly resemble those of cerous sulphate. (Beringer.)

### Lanthanum and Chlorine.

Chloride of Lanthanum.—1. The hydrochloric acid solution of the oxide evaporated and heated in a current of hydrochloric acid gas till rendered perfectly anhydrous, leaves chloride of lanthanum. (Mosander.) —2. 100 parts of oxide of lanthanum ignited in a tube through which a current of hydrochloric acid gas is passed, yield 162·09 parts of chloride of lanthanum. (Choubine.) Chloride of lanthanum is very soluble in water (Mosander); the solution yields pale rose-coloured, hydrated crystals (Beringer); perfectly white when pure. (W.)

### Lanthanum and Nitrogen.

Nitrate of Lanthanum.—Very soluble in water. (Mosander.) ¶ Readily soluble also in alcohol. Crystallizes in deliquescent colourless prisms. The solution evaporated at a temperature above 30°, yields an opaque white mass. When carefully heated, so that water is alone expelled, it fuses, and solidifies to a colourless glass on cooling. If the heat is raised so as to drive off a portion of the acid, a fused mass remains, consisting of neutral and basic salt. On cooling, it solidifies and forms a sort of enamel, which almost immediately afterwards crumbles to a bulky white powder, and with such force, that particles are scattered about to a distance of several inches. (Mosander, *Ann. Pharm.* 48, 210.) ¶

### Lanthanum and Potassium.

Sulphate of Lanthanum and Potash.—Sulphate of potash does not precipitate the lanthanum-salts; the double salt, however, is but sparingly soluble. (Mosander.) According to Th. Scheerer, the salts of lanthanum form red or yellow precipitates with sulphate of potash.

| | Choubine. |
|---|---|
| Potash | 27·48 |
| Oxide of Lanthanum | 25·69 |
| Sulphuric Acid | 46·68 |
| | 99·85 |

¶ Chapter IX. (A.)

# DIDYMIUM.

Mosander, *Pogg.* 56, 504; *Phil. Mag. J.* 28, 241; abstr. *Ann. Pharm.* 48, 210.
Watts, *Qu. J. of Chem. Soc.* 2, 131.

This metal was discovered by Mosander in 1841. It appears to be always associated with cerium and lanthanum, and therefore occurs in Cerite, Orthite, Monazite, &c. It has not yet been obtained in the metallic state; neither has its atomic weight been ascertained.

Oxide of Didymium.—*Preparation.* The oxides of lanthanum and didymium having been freed from cerium and converted into sulphates, the solution of the mixed sulphates is acidulated with sulphuric acid and left to evaporate in a warm place. Two sorts of crystals then separate, viz., large rose-coloured rhombohedral crystals; and slender, prismatic, violet crystals; the former, which are nearly pure sulphate of didymium, are to be picked out, and purified by recrystallization. [Mosander first separates the greater part of the sulphate of lanthanum by the process described at page 276, then acidulates the mother-liquor, and leaves it to evaporate. The crystals of sulphate of didymium may, however, be at once obtained from the original solution of the mixed sulphates, without this preliminary process.]

A pure salt of didymium having been thus obtained, the oxide may be prepared by precipitating with caustic potash or oxalate of ammonia, and igniting the precipitate.

The anhydrous oxide is of a dark-brown colour, but not uniform, some parts being lighter than others; this is particularly the case, when it has been obtained by igniting the hydrated oxide precipitated by a caustic alkali. At a white heat, it loses its brown colour and becomes dirty white. Heated with microcosmic salt in the inner blowpipe flame, it forms an amethyst-coloured glass, like that formed by titanic acid. Heated with carbonate of soda on platinum foil, it yields a mass of a greyish-white tint. The *hydrated oxide* is of a violet colour; it absorbs carbonic acid from the air, but less rapidly than hydrated oxide of lanthanum.

Salts of Didymium.—Both the hydrated and anhydrous oxides dissolve readily in acids whether concentrated or dilute. When boiled with sal-ammoniac, they are also dissolved, with evolution of ammonia, but less

readily than oxide of lanthanum. Altogether, oxide of didymium is a less powerful base than oxide of lanthanum. This circumstance may be made available for effecting a partial separation of the two oxides (*vid.* p. 275). All the salts are coloured, some being pink or rose-coloured, some amethyst or violet-coloured. The solutions are not precipitated by sulphide of ammonium, unless a large quantity is added, and the mixture afterwards heated; in that case, hydrosulphuric acid is evolved, and a red basic salt precipitated. Ammonia likewise throws down a basic salt, which may be washed without passing through the filter. Potash or soda precipitates the hydrated oxide.

*Sulphate:* Appears to belong to the doubly oblique prismatic system. (Wallmark.) Crystallizes from a solution containing lanthanum, in rhombohedral crystals with numerous secondary faces; but when these crystals are dissolved and the solution left to evaporate, small crystals are obtained, having the form of an oblique rhombic prism without secondary faces. This appears to be the form of the pure salt. (W.) Dissolves in 5 parts of water at a temperature between 15° and 20°. The anhydrous salt dissolves rapidly when thrown into water by small portions at a time. A cold saturated solution deposits the salt in crystals, at 53°, and continues to deposit a larger quantity as the temperature rises, so that at 100° C. only 1 part of the salt remains dissolved in 50·5 parts of water. It is not decomposed at a low red heat. By exposure to a white heat for an hour, it loses two-thirds of its acid. With sulphate of potash it forms an amethyst-coloured salt, which is totally insoluble in excess of sulphate of potash. (Mosander.)

*Nitrate:* Crystallizes with difficulty. Deliquescent. A strong syrupy solution of this salt has a beautiful red colour, but appears violet-blue by reflected light. It cannot be fused without loss of acid. The solidified mass does not crumble to powder like the lanthanum salt, but retains its form. (Mosander.) ¶

CHAPTER X.

# YTTRIUM.

Gadolin. Yttria. *Crell. Ann.* 1796, 1, 313.
Eckeberg. Yttria. *Scher. J.* 3, 187; also *Crell. Ann.* 1799, 2, 65.—Further: *Scher. J.* 9, 597.
Klaproth. Yttria. *Scher. J.* 5, 531.
Vauquelin. Yttria. *Scher. J.* 5, 552; also *Crell. Ann.* 1801, 1, 227.
Berzelius. Yttria. *Schw.* 16, 250 and 404, and *in his Lehrbuche.*
Wöhler. Yttrium: *Pogg.* 13, 580.
Berlin. Yttria. *Pogg.* 43, 105.
Mosander. Yttrium, Erbium, Terbium. *Ann. Pharm.* 48, 219.

*History.* Yttria was discovered in 1794 by Gadolin, and further examined by Eckeberg, Klaproth, Vauquelin, Berzelius, and Berlin. Wöhler obtained from it the metal yttrium. ¶ In 1843, Mosander discovered that the substance hitherto denominated *yttria*, and regarded as a simple earth, is in reality a mixture of three different earths, one of which in the anhydrous state is yellow, while the other two are colourless. For the strongest of these three bases the name of *Yttria* is retained, while the other two have received the names of *Erbia* and *Terbia*,—terms, which, as well as *Yttria*, are formed from the letters of the word *Ytterby*, the name of the locality where the mineral Gadolinite, the original source of all these substances, was discovered. The following descriptions of yttria and its compounds, as far as page 290, refer to the mixed earth to which that name was originally applied. ¶

*Sources.* Very rare. Combined with fluorine in Yttrocerite, and in small quantities in fluoride of cerium and in Warwickite; as carbonate of yttria; as phosphate of yttria; as silicate of yttria, together with other silicates, in Gadolinite, Orthite, Pyrorthite, and in small quantities, in Pyrochlorite and Cerite; as titanate of yttria, in Polymignite; as tantalate, in Yttrotantalite, Euxenite, and Fergusonite.

*Preparation.* Chloride of yttrium and flattened globules of potassium are arranged in alternate layers in a platinum crucible, the quantity of potassium not being quite sufficient to decompose the whole of the chloride of yttrium; the cover is then fastened down by a wire, and heat applied by means of a spirit-lamp. The reduction is effected in a moment, and with such violent disengagement of heat, that the crucible becomes white hot. When the whole has become perfectly cold, the cover is taken off, and the crucible thrown into a large glass of water, in which the fused

chloride of potassium dissolves, with evolution of a small quantity of hydrogen gas having a fœtid odour; and the yttrium is collected on a filter, washed thoroughly, and dried. (Wöhler.) Yttria is but imperfectly decomposed by vapour of potassium at a white heat. (H. Davy.) The double fluoride of yttrium and potassium appears to be decomposed by potassium; but on the addition of water, the pure yttrium which may have been separated is reoxidized. (Berzelius, *Pogg.* 4, 117.)

*Properties.* Dark-grey, shining powder, consisting of small scales, having a metallic aspect and iron-grey colour; under the burnisher, it takes the colour and lustre of iron; it appears to be brittle. (Wöhler.)

## *Compounds of Yttrium.*

### Yttrium and Oxygen.

### Yttria. YO.

*Oxide of Yttrium, Gadolinerde, Yttererde, Gadoline.*

*Formation.* Yttrium does not oxidize in the air or in water at ordinary temperatures; heated in the air nearly to redness, it burns with a dazzling light and forms a white earth; when burned in oxygen, it exhibits one of the most splendid combustions known, and leaves a white residue showing traces of fusion. Yttrium dissolves readily in aqueous acids, with evolution of hydrogen gas; with greater difficulty in solution of potash; and is insoluble in ammonia. (Wöhler.)

*Preparation.*—1. One part of Gadolinite (containing yttria, silica, protoxide of cerium and sesquioxide of iron) is digested with 10 parts of oil of vitriol and 6 parts of water, a moderate heat being applied and the liquid frequently stirred. The whole is then evaporated to dryness; the residue exhausted with water containing a very small quantity of hydrochloric acid; the solution filtered from the silica; again evaporated to dryness; and the residue ignited to decompose the iron-salt contained in it. The residue is next boiled with 24 parts of water; filtered hot from the oxide of iron; again evaporated, ignited and treated with water; and from the filtrate, after the copper and manganese have been separated by careful addition of sulphide of potassium (a larger quantity would also separate the yttria), the yttria is thrown down by ammonia in the form of hydrate, which is rendered anhydrous by ignition. (Vauquelin.) The yttria precipitated by excess of ammonia from a solution containing potash and sulphuric acid, invariably contains a portion of these two substances; ceric oxide also remains mixed with it. (Berzelius.)

2. Powdered Gadolinite is dissolved in aqua regia; the solution evaporated to dryness; the mass exhausted with hot water acidulated with hydrochloric acid; the solution filtered from the silica; mixed with a sufficient quantity of crystallized sulphate of potash, which must project above the surface of the liquid; and left to stand for a space of 24 hours: sulphate of cerous oxide and potash is then precipitated in the form of a white powder. The whole is then thrown on a filter and washed two or three times with water saturated with sulphate of potash; the filtrate and washings neutralized with ammonia; and the sesquioxide of iron precipitated by

succinate of ammonia. The filtered liquid treated with ammonia yields a precipitate consisting of basic sulphate of yttria mixed with a small quantity of protoxide of manganese: it is repeatedly digested, while still moist, with fresh quantities of a dilute solution of carbonate of ammonia, well shaken, and allowed to stand. The carbonate of yttria dissolved in this liquid is precipitated on boiling the filtrate, and then ignited. (Berzelius.) If after ignition it exhibits a brown instead of a greyish-yellow colour, it contains manganese. To get rid of this impurity, it is dissolved in nitric acid, evaporated to dryness, and heated in a sand-bath to the melting point of tin, by which means the nitrate of manganese is decomposed. The mass is then dissolved in a very small quantity of water; the almost syrupy liquid filtered through paper; diluted; mixed with ammonia; and the resulting hydrate exposed to a red heat. The residue on the filter containing manganese, yields, by washing with more water, a brown solution, which may be again evaporated and heated to separate the manganese. (Berzelius.)

3. Gadolinite is treated with aqua regia, &c., as in the second method; the solution filtered from the silica diluted largely with water; neutralized with ammonia; precipitated while hot by succinate of ammonia; and filtered rapidly (otherwise succinate of yttria will be precipitated as well as succinate of iron). The filtrate, reduced to a smaller bulk by evaporation, is then mixed, as in the second method, with sulphate of potash; the solution, separated from the double sulphate of cerous oxide and potash, digested with potash in excess; the precipitate well washed and strongly ignited (by which a large quantity of sulphuric acid still present is driven off); dissolved in dilute nitric acid, which leaves sesqui-oxide of cerium and peroxide of manganese untouched; and the filtrate mixed with just enough carbonate of soda to precipitate the earth (an excess of the alkaline carbonate would redissolve it). The carbonate of yttria, after being washed and ignited, is dissolved in dilute nitric acid; and the precipitation by carbonate of soda, ignition, and re-solution in weak acid repeated several times, the nitric acid solution being lastly evaporated to dryness and ignited; or mixed with oxalate of ammonia, and the insoluble oxalate of yttria washed and decomposed at a red heat. (Berlin.)

For the separation of yttria from sesquioxide of iron, Th. Scheerer (*Pogg.* 56, 496) recommends the following method: The acid solution is neutralized with ammonia till it becomes of a dark yellow, but not reddish-yellow colour (in the latter case the alkaline oxalate would subsequently give a yellow precipitate containing iron); a large quantity of solution of acetate of ammonia is then added to the mixture, and lastly oxalate of ammonia in sufficient quantity to throw down the whole of the yttria as a white oxalate. The latter is then washed and converted into pure yttria by ignition. (If oxalate of potash is used, a double oxalate of yttria and potash separates; this, after ignition, leaves yttria mixed with carbonate of potash, from which it cannot be completely purified by water.) In the same manner, cerium and lanthanum may be freed from sesquioxide of iron.

*Properties.* White powder, fusing but slightly at the highest temperatures, as in the combustion of yttrium. (Wöhler.) Berzelius obtained the earth of a pale greyish-yellow colour; never white, unless it retained a portion of sulphuric acid. Berlin found it to be yellowish white when in the purest possible state; the specimens prepared by igniting the hydrate were of a deeper yellow than those obtained by igniting the oxalate.

According to Th. Scheerer, also, yttria perfectly free from manganese, is yellow: it appears white, however, during ignition, and regains its yellow colour only as the heat falls below redness. Scheerer attributes this colour to the presence of oxide of didymium, which, when strongly heated loses oxygen, and at the same time its peculiar tint, but recovers it again as it cools (*vid.* p. 280).

The specific gravity of yttria is 4·842 (Eckeberg); it is destitute of taste and smell, and has no effect on vegetable colours. It is but slightly decomposed by exposure to the vapour of potassium at a white heat (H. Davy); nor is it affected by ignition with charcoal in the heat of the most powerful forge (Gadolin).

| | Calculation. | | | | Berzelius. |
|---|---|---|---|---|---|
| Y ..... | 32 | .... | 80 | ..... | 80·1 |
| O ..... | 8 | .... | 20 | ..... | 19·9 |
| YO..... | 40 | .... | 100 | ..... | 100·0 |

*Combinations.* *a.* With Water.—Hydrate of Yttria.—Chloride of yttrium or acetate of yttria is precipitated by caustic potash. By ammonia, the yttria is not completely separated, because the ammoniacal salt which is formed, retains a portion of the earth in solution. (Berlin.) From nitrate or sulphate of yttria the alkalis throw down a basic salt. (Berzelius.) The precipitate, which is very bulky, becomes milk-white and opaque when dry. (Berzelius.) It shrinks together strongly when dried, and at the same time loses its pure white appearance, and absorbs carbonic acid. (Berlin.) According to Klaproth, it contains 31 per cent. of water.

*b.* With Acids, producing the Salts of Yttria. The affinity which this earth manifests towards acids, is less than that of the alkalis or of magnesia; the hydrate of yttria, however, decomposes ammoniacal salts at a boiling heat, and dissolves. (Berzelius.) The yttria-salts are colourless. The reddish tint frequently observed in them is owing to the admixture of a salt of didymium. (Mosander.) Berlin obtained the hyposulphate, nitrate, and acetate of yttria, and the chloride of yttrium perfectly free from colour; in the sulphate only a slight shade of red was observed to exist.—The salts of yttria have a greater specific gravity than those of the other earths. The soluble salts of yttria are for the most part crystallizable, have a sweet and somewhat astringent taste, and redden litmus-paper. They part with their acid at a red heat, provided the acid is of a volatile nature. From solutions of yttria-salts, the caustic alkalis throw down a white, voluminous, flocculent precipitate, consisting partly of hydrate of yttria, and partly of a basic salt; the precipitate is not redissolved by an excess of the alkali. The alkaline sulphides produce a similar result, with evolution of sulphuretted hydrogen. (Berzelius.) According to Klaproth and Vauquelin, the monohydrosulphates of the alkalis do not affect solutions of yttria.—The carbonates of ammonia, potash, or soda precipitate the earth in the form of carbonate; monocarbonate of potash or of soda in excess redissolves the precipitate in very small quantities; sesquicarbonate of ammonia and bicarbonate of potash, in somewhat larger quantity. (H. Rose.)—Ordinary diphosphate of soda gives in a solution containing not less than one part of salt in 1000 parts of water, a white precipitate, which is soluble in hydrochloric acid, and appears again on boiling.—Sulphate of potash,

added to a rather concentrated solution of yttria, produces, after some time, a precipitate consisting of a double salt, which is perfectly soluble in a large quantity of water, even though it be saturated with sulphate of potash. (Berzelius.)—Di-arseniate of soda produces a white precipitate.—Oxalic acid throws down, even from rather acid solutions, a copious precipitate of oxalate of yttria, soluble in hydrochloric acid. Oxalate of potash precipitates double oxalate of yttria and potash. Ferrocyanide of potassium precipitates white ferrocyanide of yttrium.—Tincture of galls gives a loose, grey (Klaproth), or brown (Vauquelin) floculent precipitate. The following reagents do not affect solutions of yttrium: hydrosulphuric acid; carbonate of lime—which separates a portion of yttria, only when sesquioxide of iron is present in the liquid (Kobell, *J. pr. Chem.* 1, 92); alkaline succinates (unless in highly concentrated solutions); and ferricyanide of potassium.

## Yttrium and Carbon.

Carbonate of Yttria.—Found in the mineral kingdom.—Hydrate of yttria absorbs carbonic acid from the air. (Vauquelin.)—When a salt of yttria is precipitated with the exact quantity of carbonate of soda required, the resulting salt, after being washed and dried, has the form of a light colourless powder; but if an excess of carbonate of soda is used, the precipitate gradually changes under the supernatant liquid to small white shining crystals. Both forms have precisely the same composition: $YO, CO^2 + 3Aq.$ (Berlin.)—The salt loses $\frac{1}{3}$ of its water at 100°; the remainder at about 130°; at a red heat, the greater part of the carbonic acid is expelled; but even after exposure to a white heat for two hours, the earth still retains 2 per cent. of carbonic acid. (Berlin.)—Carbonate of yttria gradually dissolves in an aqueous solution of chloride of ammonium and other ammoniacal salts, carbonate of ammonia being set free. (Berzelius.)—It is not soluble in water, but is dissolved in very small quantities by aqueous carbonic acid. (Gadolin, Berlin.)

| | Calculation. | | Klaproth. | Berlin. |
|---|---|---|---|---|
| YO | 40 | 44·94 | 55 | 69·76 |
| $CO^2$ | 22 | 24·72 | 18 | |
| 3HO | 27 | 30·34 | 27 | 30·24 |
| $YO, CO^2 + 3Aq.$ | 89 | 100·00 | 100 | 100·00 |

## Yttrium and Boron.

Borate of Yttria.—With boracic acid yttria fuses to a white enamel. (Gadolin.) The monoborate and biborate of soda give with salts of yttria a colourless precipitate, which, while moist, is glutinous and transparent, but after drying, becomes white and solid; it attracts carbonic acid from the air during the process of washing. (Berlin.)

## Yttrium and Phosphorus.

A. Phosphide of Yttrium.—Yttrium, heated with phosphorus, inflames in its vapour and forms a blackish-grey powder, which, in contact with water, evolves spontaneously inflammable phosphuretted hydrogen

gas. (Wöhler.)—Phosphide of yttria is produced by igniting yttria in vapour of phosphorus. (Berlin.)

B. Phosphate of Yttria.—*a. Triphosphate.*—Found native, consisting of 62·58 per cent. of yttria, 33·49 of phosphoric acid (with a small quantity of fluorine), and 3·93 of basic phosphate of ferric oxide. (Berzelius.)—1. Formed by mixing a salt of yttria with phosphoric acid and precipitating by ammonia.—2. Separated by boiling a saturated solution of the salt *b* in hydrochloric acid.—The washed, translucent, gelatinous precipitate absorbs carbonic acid, whilst drying, till it is converted into a mixture of carbonate and diphosphate of yttria. Before ignition, it is easily soluble, but after ignition, difficultly soluble in acids. A solution of the salt in hydrochloric or nitric acid deposits it, after evaporation, as an opaque, white, insoluble residue; a solution in sulphuric acid deposits the salt on evaporation, in a crystalline form, so that the concentrated acid no longer retains any of it in solution; the crystals partially dissolve in water [as sulphate of yttria?], whilst a skeleton mass of diphosphate of yttria remains behind. (Berzelius.)

*b. Diphosphate.*—Formed by precipitating a salt of yttria with ordinary diphosphate of soda.—White powder, infusible before the blowpipe. (Gadolin.) A saturated solution of this salt in hydrochloric or nitric acid deposits the salt *a*, on boiling. (Berzelius.)

*c. Acid phosphate.*—Prepared by dissolving *b* in phosphoric acid. Has a rough, acid taste, and yields a jelly by evaporation. (Gadolin.)

## Yttrium and Sulphur.

A. Sulphide of Yttrium.—Yttrium heated with sulphur, takes fire as soon as the sulphur begins to volatilize, and burns, forming grey pulverulent sulphide of yttrium, which is neither dissolved nor acted on in any way by water, but when digested in aqueous acids, evolves hydrosulphuric acid in abundance. (Wöhler.)

B. Sulphite of Yttria.—Formed by treating hydrate of yttria with an aqueous solution of sulphurous acid, or by precipitating a salt of yttria by an alkaline sulphite.—White powder, insoluble in pure water, but sparingly dissolved by water saturated with sulphurous acid; this solution left to evaporate spontaneously in the air, deposits crystals of sulphate of yttria. (Berlin.)

| | Calculation. | | | | Berlin. |
|---|---|---|---|---|---|
| YO | 40 | .... | 55·56 | .... | 55·57 |
| $SO^2$ | 32 | .... | 44·44 | .... | 44·43 |
| YO, $SO^2$ | 72 | .... | 100·00 | .... | 100·00 |

C. Hyposulphate of Yttria.—A solution of yttria in the aqueous acid, evaporated spontaneously to the thickness of syrup, yields long, clear, brilliant, rectangular, obliquely truncated prisms, which, like the solution, evolve sulphurous acid, even at 100°. (Berlin.)

D. Sulphate of Yttria.—*a. Trisulphate.*—Formed by igniting the normal sulphate of yttria, or by precipitating an aqueous solution of it by excess of ammonia. White powder, which loses the whole of its

acid by prolonged exposure to a strong red heat. Insoluble in water. (Berzelius.) Potash, even in excess, throws down a basic salt from a solution of the sulphate. When the nitric acid solution of the basic salt is evaporated, normal sulphate of yttria crystallizes out, whilst nitrate of yttria remains dissolved in the acid mother-liquor. (Berlin.)

*b. Monosulphate.* The earth dissolves in sulphuric acid, with evolution of heat. (Vauquelin.)—Small, dense, pale amethyst-coloured, oblique four and six-sided prisms, with four-sided summits; permanent in the air (Ekeberg); specific gravity 2·79; taste sweet, but afterwards rough. —The salt begins to effloresce at 40°, and becomes milk-white, but still retains its form; does not recover its transparency by immersion in water. (Berzelius.) At a red heat, or when mixed with excess of ammonia, it loses $\frac{2}{3}$ of its acid, and is converted into the salt *a*. (Berzelius.) —Dissolves very slowly in 25—30 parts (Klaproth); in 50 parts (Vauquelin) of cold water, and in a not much smaller quantity of hot water. In water containing sulphuric acid, it is still less soluble than in pure water: hence, an excess of sulphuric acid in the solution favours the crystallization of the salt. (Berzelius.)

## Yttrium and Selenium.

A. Selenide of Yttrium.—Yttria, heated with selenium to the melting point of the latter, combines with it—the act of union being attended with slight incandescence. The result is a black mass, which is not decomposed by pure water, but evolves hydroselenic acid on the addition of dilute acids. (Wöhler.)—The double selenide of hydrogen and ammonium gives flesh-coloured precipitates with salts of yttria. (Berzelius.)

B. Selenite of Yttria.—The normal alkaline selenites precipitate from salts of yttria, large, colourless, curdy flakes, forming, when dry, a white powder, which, on exposure to heat, loses, first water, and then the whole of its acid, and is not soluble either in water or in excess of selenious acid. (Berzelius.)

## Yttrium and Iodine.

A. Iodide of Yttrium.—The aqueous solution yields, by spontaneous evaporation, small transparent crystals, apparently of the form shown in *Fig.* 15. Evaporated by heat, it leaves a deliquescent saline mass. The crystals, when ignited in the air, yield a compound of iodide of yttrium and yttria. They are very soluble in water, and slightly soluble in alcohol. (Berlin.)

B. Iodate of Yttria.—Separates in the form of a white powder, or is deposited on evaporating a solution in nitric acid, as a white anhydrous crust, which adheres to the sides of the vessel. Ignited in the air, it is decomposed with explosion and incandescence, vapour of iodine and oxygen gas being set free. It is soluble in 190 parts of water. (Berlin.)

### Yttrium and Bromine.

A. Bromide of Yttrium.—A solution of yttria in aqueous hydrobromic acid yields, on evaporation, a syrupy liquid, from which small deliquescent cubes are deposited. (Berlin.) An aqueous solution of bromine acts slightly on yttria, forming small quantities of bromide of yttrium and bromate of yttria. (Berlin.)

B. Bromate of Yttria.—Resembles the iodate. Leaves bromide of yttrium after ignition. When mixed with charcoal or sulphur, it does not explode on being struck with a hammer. It is more soluble in water than the iodate. (Berlin.)

### Yttrium and Chlorine.

A.—Chloride of Yttrium.—Dry chlorine gas is passed over a mixture of yttria and charcoal ignited in a tube of glass or porcelain. The chloride of yttrium sublimes in white shining needles, which, near the ignited portion of the tube, fuse to a white crystalline mass. Decomposed by potassium. (III. 282.) (Wöhler.) If the yttria employed has been precipitated by excess of ammonia from a liquid containing sulphuric acid and potash, it yields, when treated with charcoal and chlorine (in consequence of its retaining a portion of the sulphuric acid and potash), a dark-red, viscid mixture of chloride of sulphur and chloride of yttrium, and afterwards a sublimate of pure chloride of yttrium. In the charcoal there remains a compound of chloride of yttrium and chloride of potassium, forming an efflated, crystalline mass, which does not evolve chloride of yttrium, even when strongly ignited. (Wöhler.) [H. Rose (*Pogg.* 59, 101) states that no chloride of yttrium can be obtained by the use of chlorine and charcoal.]

*Hydrated Chloride of Yttrium*, or *Hydrochlorate of Yttria*.—Chloride of yttrium dissolves in water with considerable elevation of temperature, and likewise deliquesces very rapidly in the air. (Wöhler.) The same solution is obtained on dissolving yttria in hydrochloric acid. The liquid, when spontaneously evaporated in the air, yields, after some time, small transparent, very soluble crystals, of tabular form. (Berlin.) When evaporated in a warm place, it leaves a gummy, deliquescent mass, which is very difficult to dry thoroughly, and melts at a gentle heat. (Gadolin, Vauquelin.) When ignited, it evolves hydrochloric acid and leaves pure yttria. (Berzelius.)

### Yttrium and Fluorine.

A. Fluoride of Yttrium.—Found in an impure state in *Yttrocerite*, and in native *Fluoride of Cerium*. By precipitating hydrated chloride of yttrium with fluoride of potassium, hydrated fluoride of yttrium or hydrofluate of yttria is obtained in the form of a white powder (Gay-Lussac & Thénard), having a rough taste, and reddening moistened litmus-paper; it is not soluble in water or in aqueous hydrofluoric acid. By ignition it is converted, with loss of water, into anhydrous fluoride of yttrium, which is tasteless and has no action on litmus-paper. (Berzelius, *Pogg.* 1, 23.)

B. Fluoboride of Yttrium, and Hydrofluate of Borate of Yttria.—Soluble only in water containing excess of acid, from which it crystallizes on evaporation. (Berzelius.)

### Yttrium and Nitrogen.

A. Nitrate of Yttria.—A concentrated solution yields, after long standing, large colourless crystals (Berzelius); evaporated at 50° and then rapidly cooled, it crystallizes in colourless plates. (Berlin.) Ekeberg obtained by evaporation a fibrous mass; Klaproth, a viscid mass; and Vauquelin, by continuing the evaporation still further, obtained a mass of the consistence of honey, which, on cooling, became as hard as stone. This salt has a stronger taste than the sulphate of yttria. (Vauquelin.) By exposure to the air, it softens and deliquesces. (Ekeberg.)

B. Carbonate of Yttria and Ammonia.—Carbonate of yttria dissolves in an aqueous solution of carbonate of ammonia more readily than the protoxide of cerium; it requires, however, according to Vauquelin, about five or six times as much of the solvent as the carbonate of glucina. The presence of protoxide of cerium, or of sesquioxide of iron in very small quantities, renders the carbonate of yttria nearly insoluble in carbonate of ammonia. (Berlin.) From an over-concentrated solution, the double carbonate of yttria and ammonia separates after the lapse of twenty-four hours, as a white powder, which is not dissolved by excess of carbonate of ammonia. (Berzelius.) The solution is decomposed by the application of heat, or by the addition of an acid.

### Yttrium and Potassium.

A. Carbonate of Yttria and Potash.—Carbonate of yttria dissolves in an aqueous solution of carbonate of potash, but with greater difficulty than in a solution of carbonate of ammonia.

B. Sulphate of Yttria and Potash.—Prepared by mixing the two simple salts.—Crystalline grains, less soluble in water than the sulphate of yttria, but more so than the double sulphate of cerous oxide and potash. (Gahn & Berzelius.) The compound salt is made up of the two simple salts in equal numbers of atoms. It is soluble in 16 parts of cold water; in 10 parts of water saturated with sulphate of potash; and in a still smaller quantity of the latter solution, if it likewise contains an ammoniacal salt or free acid. (Berlin.)

C. Chloride of Yttrium and Potassium.—(III. 289.) Also obtained by fusing the simple chlorides together. Dissolves in water with evolution of heat.

D. Fluoride of Yttrium and Potassium.—Appears to be decomposed by ignition with potassium; but by subsequent exposure to a white heat, it again returns to its original state, while the potassium is volatilized. (Berzelius.)

### Yttrium and Sodium.

A. Carbonate of Yttria and Soda.—An aqueous solution of carbonate of soda dissolves a small quantity of yttria, which is again thrown

down on neutralizing with an acid (Klaproth), and, when the liquid evaporates, is deposited on the vessel in the form of a white crust. (Berlin.) Carbonate of yttria is also dissolved by an aqueous solution of carbonate of soda. The earth is not fusible with carbonate of soda before the blowpipe. (Berzelius.)

B. In borax and in microcosmic salt, yttria dissolves in large quantity, forming a clear bead, which, either by flaming or by supersaturation with the earth, becomes milk-white merely by cooling. (Berzelius.)

No other combinations of yttrium are known.

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¶ It has been already stated that the substance commonly called *Yttria* is really a mixture of three distinct salifiable bases; for the strongest of which the name of YTTRIA has been retained, while the other two have received the names of ERBIA and TERBIA. The mode of separating these substances is as follows:

When ammonia is added by small quantities at a time to a solution of ordinary yttria in hydrochloric acid, and the precipitate produced by each addition is separately collected, washed, and dried, basic salts are obtained, the last of which are colourless, and consist of pure *yttria*. And proceeding from these last in the reverse order, we find that the precipitates become reddish and nearly transparent, and contain a larger and larger quantity of *terbia*, or *oxide of terbium*, while the first formed precipitates contain the largest quantity of *erbia*, or *oxide of erbium*, mixed however with terbia and yttria.—When a solution of crude yttria in nitric acid is treated in the same manner, and the several precipitates separately heated, the first precipitate yields an oxide of a deep yellow colour; and the colour of those which follows becomes continually lighter, till at length a colourless oxide is obtained, consisting mainly of yttria mixed with a small quantity of terbia. In these experiments, it is important that the crude yttria should be perfectly free from iron, uranium, &c. It is better, therefore, to precipitate it from the original solution by a dilute solution of sulphide of ammonium; and, when the precipitate ceases to exhibit a bluish green tinge, to filter the solution, and proceed with the filtrate as above. Or better still: to add a portion of free acid to the solution of yttria, and then to drop it gradually into a solution of binoxalate of potash, stirring constantly, till the precipitate no longer redissolves. In a few hours a precipitate is deposited: this must be separated by filtration, and the clear liquid again treated with binoxalate of potash, as long as a precipitate continues to form. The filtrate, on being neutralized with an alkali, yields a small quantity of nearly pure oxalate of yttria. The precipitates first obtained are crystalline, and rapidly fall to the bottom of the vessel; whereas the last, which is pulverulent, is slowly deposited. The first contain the largest quantity of erbia mixed with terbia and yttria; the next, chiefly terbia contaminated with erbia and yttria; and the last, nearly pure yttria. The first precipitates are always reddish; the last colourless. If the mixture of the earths be precipitated by an oxalate, and the precipitate digested in very dilute sulphuric acid (1 part acid to 49 parts water), the acid first dissolves out the yttria, properly so called; and on treating the residue with successive portions of fresh acid, the quantity dissolved becomes less and less; and at the same time, the undissolved portion becomes more

and more yellow by calcination. When the yttria has been thus removed, the residual oxalate is to be washed and ignited; the earth which remains, dissolved in nitric acid; and the solution—which should not be too dilute—mixed to saturation with pounded sulphate of potash. By this means the erbia is precipitated in the form of a double sulphate of erbia and potash, which is nearly insoluble in water saturated with sulphate of potash, but dissolves easily in pure water. The double sulphate of terbia and potash remains in solution. The liquid having been filtered, and the precipitate washed, the sulphate of erbia and potash may be dissolved in water, and the erbia precipitated by caustic potash, then washed and ignited. The terbia may also be precipitated by treating the filtrate with caustic potash.

*Yttria*, properly so called, is a colourless earth, milk-white after ignition. By contact with a small quantity of a concentrated acid, it becomes strongly heated and dissolves, though not so quickly as in dilute acids. Its neutral solutions taste sweet at first, afterwards astringent. *Sulphate of Yttria* crystallizes in small, compact, colourless prisms, without the faintest tinge of amethyst. It retains its water of crystallization at temperatures as high as 80° (176° F.); but, when heated over a spirit-lamp, it loses water, and becomes milk-white.—*Nitrate of Yttria* is deliquescent; its solution, when highly concentrated, forms a thick syrup, which, as it cools, yields lamellated crystals.—*Chloride of Yttrium* is not volatile. A solution concentrated to the consistence of a syrup yields, by spontaneous evaporation, a radiated mass of crystals, which slowly deliquesce in the air.

*Terbia*, or *Oxide of Terbium*, has not yet been obtained in a state of perfect purity. Its behaviour with acids is similar to that of yttria. Its salts have a saccharine and astringent taste. In the solid state, they have an amethyst colour, which, however, is not constant.—*Sulphate of Terbia* forms crystals larger than those of sulphate of yttria; they effloresce at about 50° (122° F.), becoming milk-white, but not falling to powder. *Nitrate of Terbia:* The solution, when evaporated, almost always acquires a reddish tinge before it begins to crystallize. It solidifies in a radiated mass of crystals which have a decided rose-colour, and are not deliquescent.

*Erbia*, or *Oxide of Erbium*, obtained by calcination of the basic nitrate or of the hydrate precipitated by potash, is of a deep yellow colour: when obtained by calcining the oxalate or the neutral nitrate, its colour is much lighter, because it is more finely divided. When ignited in an atmosphere of hydrogen, it yields a small quantity of water, and becomes colourless. If it be afterwards gently ignited, it recovers its former colour, but increases very little in weight. Forms colourless solutions with acids. Dissolves in hydrochloric acid without perceptible evolution of chlorine.—*Sulphate of Erbia* is colourless, has a saccharine taste, and crystallizes like the sulphates of yttria and terbia; but it does not effloresce at 80°, not even when kept at that temperature for a week. *Nitrate of Erbia* also resembles the nitrates of the other two earths; but its solution does not become coloured by concentration,—the radiated crystals in which it solidifies are usually colourless, but sometimes have a reddish tinge; they are not deliquescent. (Mosander, *Ann. Pharm.* 48, 219; Berzelius, *Traité de Chimie*, Paris, 1846, 2, 167—171.) ¶

CHAPTER XI.

# GLUCINUM.

Vauquelin. Glucina. *Scher. J.* 1, 341; also *Crell. Ann.* 1798, 2, 422; also *Scher. J.* 1, 590.
Klaproth. Glucina. *Beiträge* 3, 215 and 221.
Berzelius. Glucina. *Schw.* 15, 296.
Wöhler. Glucinum. *Pogg.* 13, 577.
C. G. Gmelin. Glucina. *Pogg.* 50, 175.
Count F. von Schaffgotsch. Glucina. *Pogg.* 50, 183.
Awdejew. Glucina. *Pogg.* 56, 101.

*Glycium, Beryllium.*

*History.* Vauquelin discovered Glucina in 1798. Wöhler and Bussy, in 1828, succeeded in obtaining the metal from it.

*Sources.* Rare; found pure, as silicate of glucina, in Phenakite, and together with other silicates, in Beryl, Euclase, Leucophane, Chrysoberyll, Helvite, and in several varieties of Gadolinite.

*Preparation.*—1. From the chloride of glucinum, by means of potassium, exactly in the same manner as yttrium. (Wöhler; III., 282.) Bussy adopts a similar method. (*J. Chim. med.* 4, 455: also *Schw.* 54, 241.)—2. When Becquerel exposed a concentrated solution of chloride of glucinum mixed with a small quantity of protochloride of iron, to the influence of the electric current, in the same way as the chloride of magnesium (III., 222), glucinum contaminated with iron was first deposited—and afterwards the pure metal, in brilliant, steel-grey, crystalline laminæ.—3. Vapour of potassium passed over glucina in a platinum tube, at a white heat, yields a mixture of potash, glucina, and a dark-coloured substance having the metallic lustre; this, when heated in the air, assumes an earthy appearance; and when put into water, slowly evolves hydrogen gas, and is converted into glucina. (H. Davy, *Gilb.* 37, 186.)—4. Potassium behaves with the double fluoride of glucinum and potassium, just as with the corresponding yttrium compound. (Berzelius.)

*Properties.* Dark grey powder, receiving a metallic lustre under the burnisher; very difficult of fusion. (Wöhler.) Black mass, interspersed with shining points. (Bussy.) Steel-grey scales. (Becquerel.)

The atomic weight of glucina, assumed by Berzelius to be = 25·7 (whence that of glucinum would of course be 17·7), has been reduced, in accordance with the more recent investigations of Awdejew, to half that amount, or still later, to 12·647: hence the atomic weight of glucinum must be 4·647, or in round numbers = 4·7.

## *Compounds of Glucinum.*

### Glucinum and Oxygen.

### Glucina. GO.

*Oxide of Glucinum, Glycinerde, Beryllerde, Smaragderde, Süsserde, Glycine.*

*Formation.* Glucinum does not attract oxygen from the air at ordinary temperatures; but when ignited, it burns with vivid combustion, and forms a white earth; in oxygen gas, the combustion is most splendid; the resulting earth shows no trace of fusion. If the glucinum contains any hydrate of glucina, a flame is visible on burning it in oxygen, arising from the hydrogen gas set free. (Wöhler.) According to Bussy, glucinum, when heated in an open vessel, is converted into glucina; but the oxidation is difficult and takes a long time. Glucinum remains unchanged in water, either cold or boiling, and also in solution of ammonia; but in cold dilute nitric acid, it dissolves, with evolution of nitric oxide; in warm oil of vitriol, with evolution of sulphurous acid; and in dilute sulphuric or hydrochloric acid, as also in a solution of caustic potash, with evolution of hydrogen gas. (Wöhler.)

*Preparation.*—1. Vauquelin fuses 1 part of finely divided beryl with 3 parts of hydrate of potash (or carbonate of potash or soda, at a higher temperature); digests the mass with dilute hydrochloric acid; evaporates to dryness; heats the residue with water containing hydrochloric acid; filters the liquid from the silica; precipitates the hydrates of glucina and alumina (together with oxide of iron) from the filtrate by ammonia; washes the precipitate, and dissolves it in sulphuric acid; mixes the solution with sulphate of potash; suffers the alum which forms to crystallize out; supersaturates the mother-liquor—containing the whole of the glucina, together with a portion of alumina—with a very large quantity of carbonate of ammonia; keeps the mixture for some days in close vessels, frequently shaking it up; filters the solution—which contains carbonate of glucina dissolved in the excess of carbonate of ammonia—from the hydrate of alumina and sesquioxide of iron; boils the filtrate till the carbonate of ammonia is expelled, and the carbonate of glucina precipitated; collects the latter on a filter; washes it thoroughly; and ignites it to drive off carbonic acid. It is best to add ammonia after boiling the solution in carbonate of ammonia; because, during the boiling, the glucina may have been partially redissolved, in consequence of the ammoniacal salts contained in the liquid being decomposed.

2. Berzelius fuses the beryl with 3 parts of carbonate of potash; proceeds in the same manner as Vauquelin; but (without first removing the greater part of the alumina in the form of alum) digests the hydrates of alumina and glucina precipitated by ammonia, while they are still moist and freshly precipitated—with excess of an aqueous solution of carbonate of ammonia, frequently agitating the mixture; then filters and boils.

3. Berthier makes a mixture of equal parts of powdered beryl and marble; compresses it strongly into a crucible; heats it in a blast-furnace; takes it out as soon as it is well fused (otherwise the crucible itself would be attacked); reduces the mass to fine powder; digests it in hydrochloric acid, whereby the silica is separated in the gelatinous state; and proceeds with the filtrate as in the first and second methods. Or he dissolves the mixed hydrates of glucina and alumina (also containing sesquioxide of iron) in potash; filters from the oxide of iron; slightly supersaturates the filtrate with hydrochloric acid; precipitates both the earths with ammonia; washes them thoroughly; dissolves them in an aqueous solution of sulphurous acid; and boils the clear liquid till the excess of acid is expelled. The sulphite of alumina separates, while the sulphite of glucina remains dissolved, and may then, after filtration, be precipitated by ammonia. (*Ann. Chim. Phys.* 50, 371.)

*Properties.* Soft, light, very bulky, white powder, of specific gravity 2·967 (Ekeberg); neither hardening nor shrinking by heat; fusible only at the highest temperatures that can be produced. (H. Davy.) Tasteless; adheres strongly to the tongue.

Calculation, according to Awdejew.

| | | | |
|---|---|---|---|
| G | 4·7 | | 37·01 |
| O | 8·0 | | 62·99 |
| GO | 12·7 | | 100·00 |

*Decomposition.* At a white heat by potassium; and in the presence of iron, by charcoal also.

*Combinations.* *a.* With water: Hydrate of Glucina.—Obtained by precipitating a soluble salt of glucina by an alkali. The hydrate precipitated by ammonia perfectly resembles the hydrate of alumina while moist, but is reduced to a white powder when dry. When strongly heated, it parts with its water; without, however, becoming incandescent. (Count Schaffgotsch.)

| | Calculation. | | | Or? | Dried at 100°. | | | Shaffgotsch. |
|---|---|---|---|---|---|---|---|---|
| GO | 12·7 | .... | 58·52 | 3GO | 38·1 | .... | 51·42 | .... 51·5 |
| HO | 9·0 | .... | 41·48 | 4HO | 36·0 | .... | 48·58 | .... 48·5 |
| GO, HO | 21·7 | .... | 100·00 | | 74·1 | .... | 100·00 | .... 100·0 |

*b.* With acids, forming the Glucina-salts.—Glucina after ignition dissolves slowly but completely in acids; the hydrate dissolves with ease. The affinity of glucina for acids is less powerful than that of the alkalis, or of magnesia and yttria; but the hydrate of glucina, when boiled with ammoniacal salts, decomposes them and replaces the ammonia in the solution. (Berzelius.) The salts of glucina are colourless, unless the acid itself is coloured. Most of them are soluble in water. Those which are soluble have a sweetish, rough taste, and redden litmus. They

lose their acid on ignition, unless it is incapable of volatilization. From the solution of a glucina-salt, caustic ammonia, potash, or soda throws down the hydrate, as a bulky floculent precipitate. Alkaline sulphides act in the same manner, evolving sulphuretted hydrogen. The precipitated hydrate is re-dissolved by excess of potash or soda, from which solution sal-ammoniac again precipitates it. Ammonia in excess does not dissolve it. The alkaline earths, and likewise magnesia and yttria, throw down glucina in the form of hydrate. The normal carbonates and bicarbonates of potash and soda throw down a bulky precipitate of carbonate of glucina, soluble in a large excess of the alkaline carbonates. Carbonate of ammonia produces a similar result; but a much smaller quantity of it is sufficient to re-dissolve the precipitate. (Vauquelin.) Carbonate of baryta partially separates glucina by digestion, but almost completely on boiling. (Awdejew.) Ordinary diphosphate of soda throws down from the salts of glucina a white floculent precipitate. The salts mixed warm with fluoride of potassium till a precipitate just begins to appear, deposit, on cooling, crystalline scales of a difficultly soluble double salt. (Berzelius.) Ferrocyanide of potassium produces no change at first, but the liquid becomes gelatinous after a while. (H. Rose.) Alkaline succinates give a white precipitate with salts of glucina. Tincture of galls throws down yellow flakes from solutions of glucina-salts. (Vauquelin.)

The salts of glucina are not precipitated by hydrosulphuric acid, sulphate of potash, hydro-fluosilicic acid, carbonate of lime (Von Kobell, *J. pr. Chem.* 1, 92), oxalic acid, alkaline oxalates and tartrates, or by ferricyanide of potassium. The statement of Persoz (*Chim. Moleculaire* 388) that the salts of glucina are precipitated by heating with acetate of soda, is not confirmed by the author's experiments, at least in the case of the chloride of glucinum.

c. With Potash and Soda.

## Glucinum and Carbon.

Carbonate of Glucina.—Hydrate of glucina absorbs carbonic acid when exposed to the air. (Vauquelin.) The salt is precipitated: 1. When the double carbonate of glucina and ammonia is heated.—2. When a salt of glucina is decomposed by an alkaline carbonate not added in excess. Prepared by the first method, it is granular, and falls rapidly to the bottom of the vessel (Berzelius); when prepared by the second, it is bulky. (Count Schaffgotsch.) Soft and unctuous to the touch; tasteless. Gives up its carbonic acid when ignited; not perceptibly soluble in aqueous carbonic acid, but readily dissolved by alkaline carbonates. (Vauquelin.) Dissolves when boiled in aqueous solutions of ammoniacal salts, carbonate of ammonia being set free. (Berzelius.)

| | Calculation. | | Schaffgotsch. |
|---|---|---|---|
| 5GO | 63·5 | 48·66 | 47·53 |
| $CO^2$ | 22·0 | 16·86 | 17·57 |
| 5HO | 45·0 | 34·48 | 34·90 |
| 5GO, $CO^2$, 5HO | 130·5 | 100·00 | 100·00 |

### Glucinum and Phosphorus.

A. Phosphide of Glucinum.—Glucinum heated in vapour of phosphorus burns with a bright flame and forms a grey powder, which, on the addition of water, evolves spontaneously inflammable phosphuretted hydrogen. (Wöhler.)

B. Hypophosphite of Glucina.—An aqueous solution of hypophosphorous acid is saturated in the cold with hydrate of glucina, and the filtrate left to evaporate in vacuo over oil of vitriol. A thick viscid mass remains, which, when exposed to the air, dries up to a hard substance having a conchoidal fracture. (H. Rose, *Pogg.* 12, 86.)

C. Phosphite of Glucina.—Phosphite of ammonia gives with chloride of glucinum a white precipitate, which, on being heated in a retort after drying, becomes incandescent and evolves hydrogen gas free from phosphorus. (H. Rose, *Pogg.* 9, 40.)

D. Phosphate of Glucina.—*a. Diphosphate.*—Formed by precipitating a salt of glucina with excess of ordinary diphosphate of soda. White viscid precipitate, fusing before the blowpipe to a clear bead, which remains transparent after cooling. Insoluble in water, but dissolved by aqueous acids, including phosphoric acid. (Vauquelin.)

*b.* The *acid phosphate* is obtained by dissolving the neutral salt in an aqueous solution of phosphoric acid.

### Glucinum and Sulphur.

A. Sulphide of Glucinum.—Glucinum heated with sulphur till the latter is completely volatilized, combines with it—giving rise to vivid combustion—and forms a grey, unfused mass, which dissolves in water very slowly, without any escape of hydrosulphuric acid, but evolves that gas in abundance when treated with aqueous acids. (Wöhler.) Sulphate of glucina decomposed at a red heat with hydrogen or hydrosulphuric acid gas, does not yield any sulphide of glucinum, but only pure glucina. (Wöhler.) On heating glucina with sulphur, the earth remains behind undecomposed. (Vauquelin.)

B. Sulphite of Glucina.—Hydrate of glucina is very soluble in sulphurous acid, and is not precipitated on boiling the solution (this character distinguishes it from alumina). (Berthier, *Ann. Chim. Phys.* 50, 371.)

C. Sulphate of Glucina.—*a. Sexbasic Sulphate.*—A concentrated solution of normal sulphate of glucina is digested with freshly precipitated carbonate of glucina; the resulting solution filtered from salt *b* without adding any water; and the filtrate afterwards mixed with water: sexbasic sulphate of glucina is then precipitated, while the disulphate remains in solution. White powder, leaving 53·2 per cent. of glucina after ignition. (Berzelius.) According to Awdejew, it consists of $6GO, SO^3 + 3Aq$.

*b. Trisulphate.*—Formed during the above-mentioned digestion; dries up to a transparent, gummy mass, hard and brittle in the cold, but becom-

ing soft at 100°; when strongly heated, it is converted into a spongy, shining mass, no longer soluble in water. (Berzelius.)

*c. Disulphate.*—Obtained in the preparation of the salt *a*. Soluble in water. (Berzelius.)

| | Trisulphate. | | | Berzelius. |
|---|---|---|---|---|
| 3GO | 38·1 | 48·78 | | 49·6 |
| $SO^3$ | 40·0 | 51·22 | | 50·4 |
| 3GO, $SO^3$ | 78·1 | 100·00 | | 100·0 |

| | Disulphate. | | | Berzelius. |
|---|---|---|---|---|
| 2GO | 25·4 | 38·84 | | 39·07 |
| $SO^3$ | 40·0 | 61·16 | | 60·93 |
| 2GO, $SO^3$ | 65·4 | 100·00 | | 100·00 |

*d. Monosulphate.*—Glucina is dissolved in excess of sulphuric acid, and the excess of acid removed by evaporation and subsequent washing with alcohol. (Berzelius.) The crystalline powder thus obtained is dissolved in hot water, and yields, on cooling, tolerably large, hydrated, square-based octohedrons (*Fig.* 23), with the lateral summits slightly truncated; $e : e^1 = 122°$ nearly. The crystals effloresce at a temperature above 40°; when strongly heated, they lose water and swell up like alum. By ignition, the whole of the acid is driven off, partly undecomposed, partly resolved into sulphurous acid and oxygen gas. The residue consists of pure glucina, which however dissolves with great difficulty in sulphuric acid, and is almost insoluble in hydrochloric acid. (Awdejew.) The salt is very soluble in water; the solution reddens litmus, and, when concentrated, is of the consistence of syrup. (Berzelius.) On evaporation, the salt is deposited as a crystalline powder, without yielding a gummy mass. (Awdejew.)

| | Anhydrous. | | | Berzelius. |
|---|---|---|---|---|
| GO | 12·7 | 24·1 | | 24·33 |
| $SO^3$ | 40·0 | 75·9 | | 75·67 |
| GO, $SO^3$ | 52·7 | 100·0 | | 100·00 |

| | Crystallized. | | | Awdejew. |
|---|---|---|---|---|
| GO | 12·7 | 14·32 | | 13·87 |
| $SO^3$ | 40·0 | 45·09 | | 43·99 |
| 4HO | 36·0 | 40·59 | | 42·14 |
| + 4Aq. | 88·7 | 100·00 | | 100·00 |

Hydro-sulphocarbonate of potash gives no precipitate with chloride of glucinum. (Berzelius.)

## Glucinum and Selenium.

A. Selenide of Glucinum.—Formed on fusing together selenium and glucinum. The combination is attended with vivid combustion, and the product is a fused, brittle mass, grey and crystalline on the fractured surface. It dissolves slowly in water, without however undergoing decomposition; the solution soon becomes red from separation of selenium. (Wöhler.)—The double selenide of hydrogen and ammonium gives a flesh-coloured precipitate with salts of glucinum. (Berzelius.)

B. Selenite of Glucina. *a. Monoselenite.*—White insoluble powder, which parts with the whole of its acid at a red heat.

*b. Biselenite.*—A gummy mass, soluble in water. (Berzelius.)

### Glucinum and Iodine.

Iodide of Glucinum.—Glucinum, heated in vapour of iodine, takes fire and yields a sublimate of iodide of glucinum in colourless needles, which are fusible and very volatile, and dissolve in water with great elevation of temperature. (Wöhler.)

### Glucinum and Bromine.

Bromide of Glucinum.—Glucinum burns in vapour of bromine on the application of gentle heat, forming bromide of glucinum, which sublimes in long, colourless, fusible, very volatile needles, dissolving in water with great evolution of heat. (Wöhler.)

*Hydrated bromide of Glucinum*, or *Hydrobromate of Glucina*.—A solution of glucina in aqueous hydrobromic acid, evaporated to a small bulk and left to itself for a considerable time, yields small crystals, apparently of a cubical form, very deliquescent, and resolved by heat into hydrobromic acid gas and glucina. (Berthemot, *Ann. Chim. Phys.* 44, 394.)

Glucina diffused in water and treated with excess of bromine, is dissolved in small quantity, but does not form a bleaching liquid—bromate and hydrobromate of glucina being the only products. (Balard.)

### Glucinum and Chlorine.

Chloride of Glucinum.—Glucinum slightly heated in chlorine gas burns with a brilliant light, and forms chloride of glucinum which sublimes in a crystalline form. (Wöhler.)—The compound may be formed by passing dry chlorine gas over an ignited mixture of glucina and charcoal. (H. Rose, *Pogg.* 9, 39.) Wöhler introduces the mixture of glucina and charcoal into a glass tube, and this again into a tube of porcelain. Bussy (*J. Chim. Med.* 4, 455) ignites a mixture of glucina with sugar and starch in a covered crucible, and exposes the carbonized mass to the action of chlorine in a red-hot porcelain tube. As the glucina frequently contains sesquioxide of iron, the chloride of glucinum becomes contaminated with sesquichloride of iron. Bussy purifies it from this substance by distillation in a glass tube. The chloride of glucinum sublimes, and adheres to the colder parts of the tube in silky needles and flakes, either thickly interwoven, or caked together in a dense mass. (Rose, Wöhler.) At a gentle heat, it fuses and forms a brown liquid, which, on raising the temperature, again sublimes in colourless needles. (Rose.)—When gently heated with potassium, it is decomposed, with vivid combustion. (Wöhler, Bussy.)

| | Calculation. | | | | Awdejew. |
|---|---|---|---|---|---|
| G | 4·7 | 11·72 | 13·28 | — | 11·74 |
| Cl | 35·4 | 88·28 | 86·72 | — | 88·26 |
| GCl | 40·1 | 100·00 | 100·00 | ,, | 100·00 |

*Hydrated Chloride of Glucinum* or *Hydrochlorate of Glucina*.—Chloride of glucinum dissolves in water, with considerable elevation of temperature and a hissing noise; it also deliquesces very rapidly in the air. (Rose, Wöhler, *Bussy.*) The solution is almost perfectly transparent, the

chloride dissolving completely, with the exception of the portion which was in contact with the glass tube when softened by heat; this portion, when digested in water, deposits a small quantity of glucina in flakes. (Awdejew.)—A solution, similar in all respects, is obtained by dissolving glucina in aqueous hydrochloric acid. On evaporation, it yields an indistinct mass of crystals (Vauquelin), which, according to Awdejew, consist of GCl+4Aq. At a red heat, they part with hydrochloric acid and leave pure glucina. (Berzelius.) They are readily dissolved by water and alcohol, and do not (?) deliquesce when exposed to the air. (Vauquelin.)

When a saturated solution of glucina in hydrochloric acid is evaporated to dryness, a gummy mass remains, containing 49·135 parts (2 At.) of glucina and 50·865 parts (1 At.) of hypothetically anhydrous muriatic acid. A still more basic compound is precipitated in white flakes by boiling an aqueous solution of the above, either alone or with hydrate of glucina,—or on mixing the cold solution with a quantity of ammonia insufficient for complete saturation. (Berzelius.)

### Glucinum and Fluorine.

Fluoride of Glucinum and Hydrofluate of Glucina.—A solution of glucina in aqueous hydrofluoric acid dries up to a colourless, transparent, gummy mass, which remains clear below a temperature of 60°; gives off water at 100°, becoming milk-white and then swelling up like alum; and loses part of its acid at a red heat, unless all the water has been previously expelled. It dissolves easily in water after being heated. The solution tastes less sweet than that of any other salt of glucina. Fluoride of glucinum forms double salts with the alkalis. (Berzelius, *Pogg.* 1, 22.)

### Glucinum and Nitrogen.

A. Nitrate of Glucina.—Uncrystallizable. Obtained by evaporation, as a tenacious elastic substance, or in the form of a white powder. Its taste is very sweet at first, but afterwards astringent. It fuses readily, first becoming basic, and then losing the whole of its acid. Both water and alcohol dissolve it with great ease; it is likewise deliquescent. (Vauquelin.)

B. Carbonate of Glucina and Ammonia.—Carbonate of glucina dissolves largely in an aqueous solution of carbonate of ammonia. Colourless liquid, decomposed either by heat, or by the addition of an acid. (Vauquelin.) The hydrate of glucina precipitated by ammonia dissolves very easily in aqueous solution of carbonate of ammonia (C. Gmelin); but ignited glucina, even when digested for months in carbonate of ammonia, is but very sparingly dissolved. (Count Schaffgotsch.) Glucina, precipitated by heat from a solution in potash, is likewise nearly insoluble in carbonate of ammonia. (C. Gmelin.)

### Glucinum and Potassium.

*A. Glucina* and Potash.—The hydrate thrown down from a salt *of glucina by* ammonia, and washed either with hot or cold water, dis-

solves readily in solution of potash: so likewise the hydrate, precipitated by a small quantity of potash, is immediately redissolved on adding an excess of the reagent. (C. Gmelin.) Carbonate of glucina deposited on boiling a solution of that salt in carbonate of potash (C. Gmelin) or in carbonate of ammonia (Count Schaffgotsch), behaves in a similar manner. But glucina precipitated from a solution in potash by boiling, and then washed, is no longer dissolved by a cold solution of potash, unless it be first dissolved in an acid and reprecipitated by ammonia. (C. Gmelin.) The earth, when separated from a solution in potash by boiling, and then thoroughly washed with boiling water, is readily soluble in cold solution of potash. (Count Schaffgotsch.)

A solution of glucina in concentrated caustic potash remains clear after boiling; a weaker solution deposits a portion of the glucina on boiling; and if the liquid is very largely diluted, the whole of the glucina is separated, even below the boiling point. (C. Gmelin.) If a solution in somewhat concentrated caustic potash becomes turbid after continued boiling, an addition of water will produce a precipitate; when the liquid is somewhat dilute, the precipitation by boiling is almost complete: but if the dilution is carried beyond a certain point, the liquid must be boiled for a considerable time, to effect a perfect separation of the glucina. The earth precipitated by boiling is but very slightly redissolved as the liquid cools; if, however, only a few flakes are deposited, they are dissolved again as the liquid cools, and reappear on boiling; and this effect may be repeated again and again. (Count Schaffgotsch.) Acids and ammoniacal salts precipitate the glucina; the former, however, if added in excess, dissolve it again.

B. Carbonate of Glucina and Potash.—Carbonate of glucina is dissolved by an aqueous solution of carbonate of potash. But glucina precipitated from its solution in potash by boiling (C. Gmelin), and likewise ignited glucina (Schaffgotsch), are insoluble in carbonate of potash. The solution obtained by supersaturating chloride of glucinum with carbonate of potash, deposits less glucina on boiling, in proportion as it is more concentrated; but even when largely diluted, it does not deposit the whole of the earth. The precipitate, after thorough washing—an operation attended with difficulty, because the precipitate fills up the pores of the filter—consists of pure hydrate of glucina, free from potash and carbonic acid, but perfectly soluble in cold solution of potash; it is therefore different from the hydrate precipitated from a solution in caustic potash by boiling. (C. Gmelin.) The liquid mixed with a moderate quantity of any acid deposits carbonate of glucina.

C. Sulphate of Glucina and Potash.—When an aqueous solution of 14 parts (1 At.) of sulphate of potash, and 15 parts (rather more than 1 At.) of crystallized sulphate of glucina is evaporated at a gentle heat, the double salt is deposited in the form of a crystalline crust. The excess of sulphate of glucina is removed by cold water. The evaporation must be stopped before the liquid becomes turbid; or else the double salt will be decomposed, and the whole will solidify on cooling, to an easily soluble mixture of the two simple salts. The double salt dissolves in water very slowly, but in considerable quantity. At a red heat, it is but partially decomposed, so that water dissolves the sulphate of potash, together with a portion of the sulphate of glucina, leaving a residue of pure glucina. (Awdejew.)

| | Crystallized. | | Awdejew. |
|---|---|---|---|
| KO | 47·2 | 29·89 | 30·10 |
| GO | 12·7 | 8·05 | 8·08 |
| $2SO^3$ | 80·0 | 50·66 | 49·75 |
| 2HO | 18·0 | 11·40 | 12·07 |
| $KO, SO^3 + GO, SO^3 + 2Aq.$ | 157·9 | 100·00 | 100·00 |

D. Fluoride of Glucinum and Potassium, and Hydrofluate of Glucina and Potash.—1. On mixing chloride of glucinum with excess of fluoride of potassium, a gelatinous precipitate is formed; and when this precipitate is dissolved in hot water and the solution cooled, the salt is obtained in small scaly crystals. (Berzelius.)—2. A solution of glucina in aqueous hydrofluoric acid mixed with a solution of fluoride of potassium, yields, on evaporation, similar scaly crystals, which may be purified by recrystallization. (Awdejew.) The crystals are anhydrous, decrepitate in the fire, and dissolve with difficulty in water (Awdejew); much more freely in hot than in cold water. (Berzelius.) Gay-Lussac & Thénard originally regarded this salt as hydrofluate of glucina.

| | Crystallized. | | Awdejew. |
|---|---|---|---|
| K | 39·2 | 48·22 | 47·49 |
| G | 4·7 | 5·78 | 5·75 |
| 2F | 37·4 | 46·00 | |
| KF, GF | 81·3 | 100·00 | |

## Glucinum and Sodium.

A. Glucina and Soda.—Hydrate of glucina dissolves in solution of caustic soda.

B. Carbonate of Glucina and Soda.—Carbonate of glucina dissolves in an aqueous solution of carbonate of soda. 100 parts of ignited glucina, fused for an hour and a half with excess of dry carbonate of soda, do not expel more than from 8·73 to 9·53 parts of carbonic acid; on the addition of water, $\frac{1}{6}$ of the earth remains undissolved: the portion which is taken up is gradually precipitated by the carbonic acid of the air. (Count Schaffgotsch.) Before the blowpipe, glucina behaves with carbonate of soda, borax, and phosphate of soda and ammonia, in the same manner as yttria. (Berzelius.)

## Glucinum and Lithium.

Glucina is but very slightly soluble in an aqueous solution of carbonate of lithia. (C. G. Gmelin.)

Glucinum likewise combines with iron.

CHAPTER XII.

# ALUMINUM.

Marggraf. *Schriften*, 1, 199, 212 and 226.
Bergman: *De confectione aluminis. Opusc.* 1, 279.
Scheele: *De silice, argilla et alumine. Opusc.* 2·67; also *Crell. N. Entd.* 3, 174.
Theodore von Saussure. Alumina. *J. Phys.* 52, 290; also *Scher. J.* 7, 444.
Clement & Desormes, and Thénard & Roard. Alum. *Ann. Chim.* 57, 327 and 59, 58, also *N. Gehl.* 2, 364.
Wöhler. Aluminum and Chloride of Aluminum. *Pogg.* 11, 146.
Liebig. Aluminum and Alumina. *Ann. Pharm.* 17, 43.

*Alumium, Aluminium.*

*History.* Alum, which was probably known to the ancients (unless, indeed, by *alum* they understood a certain kind of vitriol), and, till the fifteenth century, was brought to Europe from the east, was regarded, even in the times of the Alchemists, as a compound of sulphuric acid with an earth. Stahl and others mistook this earth for lime; Geoffroy, in 1728, pointed out its existence in clay; and Marggraff, in 1754, proved it to be a substance having a separate existence and peculiar characters. Oerstedt (Ferussac, *Bull. d. Sc. Mathem. &c.* 1826, 275) showed how to prepare chloride of aluminum; and from this compound, Wöhler succeeded in eliminating the metal.

*Sources.* Next to silicium, aluminum is the most abundant of the light metals. It is found as pure alumina, hydrate of alumina, sulphate, and phosphate (sometimes mixed with other sulphates and phosphates), as silicate (either alone or combined with other silicates, in a vast number of minerals), and as mellitate of alumina; or in combination with glucina, magnesia, oxide of zinc, oxide of lead, and protoxide of iron; also as double fluoride of aluminum and sodium; and in very small quantities in plants, but not in animals.

*Preparation.* Eight or ten globules of potassium, of the size of peas and free from naphtha and carbonaceous matter, are placed at the bottom of a porcelain crucible, and upon them is placed an equal volume of chloride of aluminum. The cover is then fastened down with a wire, and the crucible heated over the flame of a spirit-lamp, gently at first, but more strongly after the mass has become red-hot. Potassium containing

carbon imparts this impurity to the aluminum. The potassium should not be in excess; because, in that case, on subsequently treating the mass with water, potash would be formed, and would cause the aluminum to be oxidized by the water. If too much chloride of aluminum is used, part of it volatilizes during the combustion. The crucible, which contains a blackish grey, almost perfectly fused mass, is allowed to get perfectly cold, and is then thrown into a large glass filled with cold water, so that no rise of temperature may take place. The chloride of potassium and the remaining chloride of aluminum then dissolve, with slight evolution of foul-smelling hydrogen gas; the solution is decanted from the grey pulverulent aluminum; and the latter is thrown on a filter, washed with cold water, and dried. (Wöhler.) From the intense heat developed during this process, a large quantity of the chloride of aluminum is lost before decomposition, partly by volatilization and partly by projection, especially if a platinum crucible is used. (Liebig.)

2. A very thin glass tube, from three to four lines in diameter, is slightly bent at about an inch from the sealed end; this portion of the tube is filled with chloride of aluminum; and two or three globules of potassium of the size of peas are introduced into the horizontal part and pushed up near to the bend by means of a glass rod. The chloride of aluminum is then heated gently, so that its vapour may slowly pass over the potassium, which immediately combines with the chlorine and becomes red-hot. Fresh globules of potassium are pushed in from time to time, and the process continued till the chloride of aluminum has entirely disappeared. The tube is then broken; the pieces thrown into a large quantity of cold water; and the aluminum washed, first with cold water, and afterwards with strong alcohol. The whole of the potassium required may also be introduced at first: in this case, the globules take fire one after the other. A thick glass tube is apt to crack when the combustion commences. As the moist aluminum soon loses its metallic lustre when exposed to the air, the final washing is best performed with alcohol. (Liebig.)—Sir H. Davy (*Gilb.* 37, 186), by passing vapour of potassium over alumina at a white heat, obtained small grey particles interspersed with aluminate of potash.

*Properties.* Grey powder, resembling finely divided platinum, with shining tin-white points here and there. The powder likewise becomes tin-white under the burnisher, and may be compressed in an agate mortar into larger scales, having the metallic lustre, much whiter than yttrium, and apparently somewhat ductile. In close vessels, it does not fuse on exposure to the heat of a blast-furnace sufficient to melt cast-iron; but becomes darker and less oxidable. When placed in the state of powder as a connector between a pair of hydro-electrical plates, it does not conduct the electricity. (Wöhler.) After fusion into a mass, it conducts electricity. (Tod Thomson, *Phil. Mag. J.* 7, 441.)

## *Compounds of Aluminum.*

### Aluminum and Oxygen.

### Alumina. $Al^2O^3$.

*Oxide of Aluminum, Alumine, Thonerde, Alaunerde.*—Found native and almost absolutely pure, in *Sapphire, Ruby,* and *Corundum.*

*Formation.* Aluminum does not change in dry air; but when heated to redness, it burns brightly and forms white and tolerably hard alumina; when heated in oxygen gas, it burns with a brilliancy which the eye can scarcely endure, and with so great a degree of heat, that the alumina formed by the combustion is partially fused.—Aluminum retains its polish under cold or lukewarm water; but near the boiling-point, it liberates hydrogen gas very slowly, the evolution of gas continuing for some time after the liquid has cooled. In solution of potash, even when very dilute, it dissolves very readily, liberating hydrogen gas; also in aqueous ammonia, which, under these circumstances, dissolves an extraordinarily large quantity of the alumina produced: similarly, in dilute hydrochloric or sulphuric acid. Aluminum is not attacked by cold concentrated nitric or sulphuric acid, but dissolves rapidly in hot oil of vitriol, with evolution of sulphurous acid. (Wöhler.)

*Preparation.*—1. Berzelius precipitates a hot solution of alum free from iron with excess of carbonate of potash or soda, and digests the precipitate with it for some time, in order to decompose the basic sulphate of alumina which is at first precipitated. He then washes the precipitate thoroughly to free it from adhering alkaline carbonate; dissolves it in hydrochloric acid; filters the solution, if not perfectly clear; precipitates the hydrate of alumina by ammonia; and lastly, ignites it.—2. Bucholz (*Beiträge*, 1, 74) precipitates the alum solution with excess of carbonate of soda; dissolves the washed precipitate in hot dilute nitric acid; throws down the hydrate of alumina by a second addition of carbonate of soda; and ignites it, after thorough washing with water.—By precipitating alum with ammonia, a basic sulphate of alumina is obtained.—3. Liebig mixes a solution of alum, free from all traces of iron, with excess of chloride of barium; evaporates the filtrate to dryness; ignites the residue; and dissolves out the chlorides of barium and potassium by means of water acidulated with hydrochloric acid.—4. Gay-Lussac (*Ann. Chim. Phys.* 5, 101) decomposes ammonia-alum by ignition: it must however be perfectly free from potash alum.

*Properties.* The sapphire, ruby, and corundum form crystals belonging to the rhombohedral system. Primitive form: a rather acute rhombohedron (*Fig.* 151; also *Fig.* 131, 132, 135, 137, 153, and other forms); $r^3 : r^3 = 86° 38'$; $r^1 : r^3$ or $r^3 = 93° 22'$; $p : r$ or $r^1 = 122° 50'$. (Hauy.) Specific gravity of the ruby = 3·531 (Brisson); of the sapphire = 3·562 (Muschenbroek); of corundum = 3·944 (Mohs), = 4·009 (Breithaupt). The hardest of all known bodies, except the diamond.—Artificially prepared alumina is white, and after exposure to a low red heat, becomes very light and soft to the touch (Bucholz, Liebig); but after strong ignition it cakes together, emits sparks when struck with steel, and is hardly to be scratched by an English file. Its specific gravity, after being strongly heated, is equal to 4·152, at 4° (39·2° F.) in vacuo. (Royer & Dumas.)—Both artificially prepared and native alumina fuse at high temperatures more readily than silica, and form a transparent glass.—Morveau obtained a white enamel by exposing artificially prepared alumina to a flame fed with oxygen gas. Sir H. Davy fused it in the circuit of a very powerful voltaic battery; Stromeyer, by means of Marcet's blowpipe; Clarke fused, in the oxy-hydrogen blowpipe flame, the ruby (which solidified to an opaque white globule), corundum, and also artificially prepared alumina, which yielded a yellow transparent glass.

Gaudin fused artificially prepared alumina (prepared by the fourth method) in the oxy-hydrogen flame, and obtained a transparent and colourless bead of the size of a hazel-nut, and having a cavity containing crystallized corundum. The fused alumina which remains after the combustion of aluminum in oxygen gas is yellowish, and cuts glass. (Wöhler.)

*Artificial Ruby.* First prepared by Gaudin. (*Ann. Pharm.* 23, 234; *J. pr. Chem.* 12, 448.) Thoroughly washed and recently precipitated hydrate of alumina is spread upon a watch-glass, to about the thickness of the back of a knife, and moistened with a drop or two of a moderately strong solution of bichromate of potash. The mass, after being well kneaded together, is slowly dried by the heat of a stove, and the cracks which appear are carefully filled up with more hydrate of alumina. When the whole is perfectly dry, a piece about an inch long is held by a pair of tongs in the oxy-hydrogen blowpipe flame, so that the flame may play upon its edge. In the course of a few minutes, transparent globules appear, of the colour of ruby, and hard enough to scratch quartz and topaz. (Böttger, *Ann. Pharm.* 29, 85.) Gaudin uses alumina obtained by igniting ammonia-alum, and mixes it with a small quantity of oxide of chromium: he states that artificial ruby has the colour, hardness, density, and cleavage of the native mineral. (*Comp.* Elsner, *J. pr. Chem.* 17, 175.)

Alumina has neither taste nor smell. Its powder, moistened with a dilute solution of nitrate of cobalt, and strongly ignited, assumes a beautiful blue colour.

| | Calculation. | | Berzelius. | H. Davy. |
|---|---|---|---|---|
| 2Al | 27·4 | 53·31 | 53·3 | 56 |
| 3O | 24·0 | 46·69 | 46·7 | 44 |
| $Al^2O^3$ | 51·4 | 100·00 | 100·0 | 100 |

*Decomposition.* By potassium at a white heat. By carbon in the presence of iron.—It is not affected by galvanic electricity, even with the aid of mercury (H. Davy); or by sulphide of carbon at a red heat. (H. Rose.)

*Combinations. a.* With water.—Hydrate of Alumina. *α. Monohydrate.*—Found native as *Diaspore.*—Diaspore has the form of a translucent, crystalline granular mass, of specific gravity = 3·43. Heated in a glass tube, it decrepitates violently, and crumbles into small white, brilliant scales, which evolve water when more strongly heated. (Berzelius.) It does not part with the whole of its water below a temperature of 360° (680° F.); consequently, not by boiling with oil of vitriol. (Dufrénoy.) It is not dissolved by boiling hydrochloric acid, which only extracts the ferric oxide mechanically mixed with it. (Hess, *Pogg.* 18, 255;—Dufrénoy, *J. pr. Chem.* 11, 129;—see also Children, *Ann. Phil.* 4, 146.)

| | *Diaspore.* | | Hess. |
|---|---|---|---|
| $Al^2O^3$ | 51·4 | 85·1 | 85·52 |
| HO | 9·0 | 14·9 | 14·48 |
| $Al^2O^3$, HO | 60·4 | 100·0 | 100·00 |

*β. Bihydrate of Alumina?*—Berthier (*Schw.* 34, 454) found in a native hydrate from Beaux, and Bucholz found in the hydrate precipitated from nitrate of alumina by carbonate of soda, 72 per cent. of alumina and 28 of water.

γ. *Terhydrate of Alumina.*—Found native as *Gibbsite.*—1. Hydrochlorate or nitrate of alumina is precipitated by excess of ammonia, and the gelatinous precipitate thoroughly washed and dried. If sulphate of alumina or alum is used, the resulting hydrate is contaminated with sulphuric acid. (Berzelius.)—Saussure distinguishes a spongy and a gelatinous hydrate. The former is precipitated from concentrated solutions of alumina by caustic ammonia or carbonate of ammonia, and dries up after washing, to an opaque earthy mass. The latter is precipitated from dilute solutions; and yields, on drying, a translucent, yellowish, brittle mass, with smooth conchoidal fracture, which does not adhere to the tongue, or fall to pieces in water. Like the spongy hydrate, it contains 59 per cent. of water, of which however it loses only 43 per cent. at a red heat, and 49·25 per cent. at a white heat.—According to Berzelius's supposition, this gelatinous hydrate still retains a portion of the acid from which the earth has been precipitated, and is therefore a basic salt. —Liebig, on the contrary, found the following results: When a concentrated solution of alum is treated with ammonia, the gelatinous precipitate is at first opaque; but by continued washing for a week—during which time it constantly yields sulphuric acid to the water—it becomes more and more transparent. The precipitate obtained from a dilute solution of alum is transparent from the first; and after being washed and ignited, yields a horny, dense kind of alumina; the hydrate precipitated from chloride of aluminum by ammonia behaves in a similar manner. 2. Aqueous solution of potash saturated with hydrate of alumina and kept in bottles or exposed to the air, deposits a difficultly soluble hydrate, which, after being thoroughly washed, is quite free from potash. (V. Bonsdorff.)

Gibbsite is stalactitic, translucent, fibrous, and readily dissolved by acids.—The hydrate prepared by the first method is sometimes a white, opaque, soft, friable mass, sometimes translucent and coherent; it adheres to the tongue, and forms a stiff paste with water. It is only when contaminated with ferric oxide, that it emits a smell of clay when breathed upon. At a red heat, it parts with its water, undergoing a remarkable contraction of volume. It is very soluble in acids.—The hydrate prepared by the second method consists of small crystalline grains, united into a crust of warty or lumpy form. It loses water at a red heat. It is scarcely soluble in cold sulphuric, hydrochloric, or nitric acid, and is very slowly dissolved by boiling hydrochloric acid: hot sulphuric acid, however, is a somewhat better solvent. (Bonsdorff, *Pogg.* 27, 275.)

| | Calculation. | | Torrey. *Gibbsite.* | Berzelius. *Artif.* 1. | Bonsdorff. *Artif.* 2. |
|---|---|---|---|---|---|
| $Al^2O^3$ | 51·4 | 65·56 | 64·8 | 65 | 65·35 |
| 3HO | 27·0 | 34·44 | 34·7 | 35 | 34·65 |
| $Al^2O^3$, 3HO | 78·4 | 100·00 | 99·5 | 100 | 100·00 |

*Hydrargyllite*, which occurs in regular six-sided prisms, is also a hydrate of alumina: its atomic composition is not yet known. (G. Rose, *Pogg.* 48, 564; 50, 656.)

*b.* With Acids, forming the Salts of Alumina. Alumina shows less affinity for acids than any of the earths hitherto considered. The sapphire, ruby, and corundum are insoluble in acids. (I., 38.) Artificially prepared alumina likewise dissolves with great difficulty after ignition.

—In fine powder, it is slowly dissolved by a mixture of equal parts of oil of vitriol and water, heated till a portion of the acid evaporates (Berzelius); it is also slowly dissolved by boiling hydrochloric acid, which does not act on powdered sapphire. (H. Rose, *Pogg.* 52, 595.)—By strong ignition with excess of a fixed alkali, even sapphire is rendered easily soluble in acids. The ordinary hydrate dissolves without much difficulty.—The salts of alumina are not coloured, unless the acid with which the earth is combined has a colour of its own. They are for the most part soluble in water, and often crystallizable.—The normal salts of alumina contain 3 atoms of acid to 1 atom of base, because the latter contains 3 atoms of oxygen.—The soluble salts have an acid, very astringent, and slightly sweet taste, and redden litmus strongly.—Those which do not contain a fixed acid, are decomposed at a red heat, the acid being volatilized or decomposed, and pure alumina left behind. Moistened with a dilute solution of nitrate of cobalt and then ignited, they yield a residue of a beautiful blue colour (smalt). From the soluble salts of alumina, all the alkalis and all the earths hitherto mentioned throw down a white, gelatinous, floculent hydrate of alumina; an excess of potash or soda redissolves the precipitate, which is again separated on adding sal-ammoniac. A large excess of ammonia dissolves but a very small quantity of the hydrate; sal-ammoniac dissolves none whatever. The normal carbonate, bicarbonate, or hydrosulphate of ammonia, potash, or soda—and, according to Fuchs, carbonate of lime also—precipitates hydrate of alumina, with evolution of carbonic acid or sulphuretted hydrogen; an excess of the carbonate of ammonia, potash, or soda dissolves but a very small quantity of the hydrate, but most when the solutions are very concentrated. Phosphate of soda added to a normal salt of alumina, precipitates phosphate of alumina in transparent, colourless flakes, soluble in acids or in potash. Concentrated solutions of salts of alumina, when mixed with sulphuric acid and potash or ammonia, in such proportion that the acid may predominate, yield, after a few minutes, crystals of alum. Monotungstate of soda precipitates the alumina-salts completely. (Anthon.) Mixed with sulphate and acetate or formiate of potash at the same time, they become turbid on the application of heat, from formation of a basic double salt, even though free acetic acid may be present. (Liebig.) Ferrocyanide of potassium throws down, slowly in the cold, but rapidly with the aid of heat, a white mixture—soon changing to green and blue—of hydrocyanate of protoxide of iron and hydrate of alumina, hydrocyanic acid being set free at the same time. (Ittner.) Alkaline succinates give a precipitate with solutions of salts of alumina, when not too dilute; tincture of galls throws down yellowish flakes. The salts of alumina are not precipitated by hydrosulphuric acid, hydrofluosilicic acid, oxalic acid, alkaline oxalates, or tartrates.

*c.* With all the alkalis, and with most of the other earths, forming a variety of compounds, some of which are found native. These compounds, in which the alumina plays the part of a weak acid, are called *Aluminates*.

### Aluminum and Carbon.

Carbonate of Alumina.—Alkaline carbonates added to a solution of any salt of alumina precipitate, not carbonate of alumina, but a compound of alumina with a small quantity of the alkaline carbonate. The

hydrate is, however, partially soluble in aqueous carbonic acid, and is again separated in the form of pure hydrate, on warming the solution or exposing it to the air. (Th. Saussure.)

¶ Muspratt finds that the precipitate produced by carbonate of ammonia in a solution of alum is really a carbonate of alumina, and gives the following analysis of it.

| | Calculation. | | | | Muspratt. |
|---|---|---|---|---|---|
| $3Al^2O^3$ | 153 | .... | 44·86 | .... | 44·82 |
| $2CO^2$ | 44 | .... | 12·91 | .... | 12·19 |
| 16HO | 144 | .... | 42·23 | | |
| $3Al^2O^3, 2CO^2, 16HO$ | 341 | .... | 100·00 | | |

(*Qu. J. of Chem. Soc.* 2, 216.) ¶

## Aluminum and Boron.

Borate of Alumina. — *a. Sexborate.* Formed by precipitating a solution of alum with borax. White pearly scales, soft to the touch (Beudant); very sparingly soluble in water.

*b. Acid borate.* Melts in the fire to a glass; has an astringent taste.

## Aluminum and Phosphorus.

A. Phosphide of Aluminum.—Aluminum heated to redness in vapour of phosphorus, combines with it, producing a rather vivid incandescence, and forming a greyish-black powder, which, under the burnisher, assumes a metallic lustre and dark grey colour; it smells of phosphuretted hydrogen, and, in contact with cold water, slowly evolves this gas in the non-spontaneously inflammable state; more rapidly in hot water. (Wöhler.)

B. Hypophosphite of Alumina.—An aqueous solution of hypophosphorous acid saturated with hydrate of alumina in the cold, and evaporated in vacuo after filtration, leaves a viscid residue, which, in a cold atmosphere free from moisture, dries up to a shining, brittle, gummy mass, of conchoidal fracture and not deliquescent. Heated in a retort, it evolves, first spontaneously inflammable and then non-spontaneously inflammable phosphuretted hydrogen gas, and leaves a reddish substance behind. (H. Rose, *Pogg.* 12, 86.)

C. Phosphite of Alumina.—Formed when an aqueous solution of terchloride of phosphorus neutralized with ammonia is precipitated by a solution of alum.—As long as the quantity of the latter is insufficient, the precipitate disappears again on shaking the mixture; the filtrate also yields a copious precipitate when boiled.—White powder, which, on being heated in a retort, evolves hydrogen gas and vapour of phosphorus, and leaves a colourless residue. (H. Rose, *Pogg.* 9, 39.)

D. Ordinary Phosphate of Alumina.—*a. Diphosphate.* This appears to be the constitution of *Turquoise* or *Kalaite*, which, according to John's analysis, must be regarded as $2Al^2O^3, PO^5 + 5Aq$, coloured by oxide of copper.

*b. Two-thirds Phosphate.*—Occurs in the form of *Wavellite, Lasionite,* or *Striegisane,* in right rhombic prisms, of specific gravity 2·33.—Obtained as a white precipitate resembling the hydrate of alumina, but less transparent, on mixing a solution of acid phosphate of alumina with excess of ammonia,—or a salt of alumina with phosphoric acid or phosphate of soda, and then with ammonia or acetate of ammonia. The salt imparts a bluish-green colour to the blowpipe flame. (Fuchs, *Schw.* 24, 121.)

| | *Wavellite.* | | Fuchs. | Berzelius. |
|---|---|---|---|---|
| $3Al^2O^3$ | 154·2 | 38·07 | 37·2 | 35·35 |
| $2cPO^5$ | 142·8 | 35·26 | 35·1 | 33·40 |
| 12HO | 108·0 | 26·67 | 28·0 | 26·80 |
| Hydrofluoric Acid, Lime, Sesquioxides of Iron and Manganese | | | | 3·81 |
| | 405·0 | 100·00 | 100·3 | 99·36 |

¶ According to Rammelsberg (*Pogg.* 64, 251 and 405), the gelatinous precipitate obtained on supersaturating a solution of monophosphate of alumina in hydrochloric acid with ammonia, is a three-fourths phosphate, having the composition $4Al^2O^3, 3PO^5 + 18Aq$. At 100°, three atoms of the water are driven off. ¶

According to Berzelius (*Ann. Chim. Phys.* 12, 16; *Jahresbericht,* 15, 197), fluoride of aluminum really enters into the composition of *Wavellite,* which he regards as a compound of $3(4Al^2O^3, 3PO^5 + 18Aq) + Al^2F^3$. Fuchs found no fluorine, and Erdmann (*Schw.* 69, 154) mere traces.

Carbonate of potash withdraws all the phosphoric acid from the salt after long digestion, and likewise dissolves a portion of the alumina, which, however, may be again thrown down by passing carbonic acid gas through the liquid. (Vauquelin, *Ann. Chim.* 96, 213; *Ann. Chim. Phys.* 21, 138.) Rammelsberg found, on the contrary, that phosphate of alumina was not decomposed after fourteen days' digestion with carbonate of potash, $\frac{1}{4}$ only of the phosphoric acid being removed, and the basic $\frac{3}{4}$-phosphate left.—The salt gives up but very little phosphoric acid to aqueous ammonia. It is readily dissolved by solution of potash, and precipitated unchanged from that solution by sal-ammoniac. Lime-water or chloride of calcium separates the whole of the phosphoric acid in the form of phosphate of lime, whilst alumina remains in solution, or at least may be dissolved out from the precipitate by treating it with an additional quantity of potash. A solution of silica (*Kieselfeuchtigkeit*) throws down a gelatinous double silicate of alumina and potash, leaving all the phosphoric acid in the liquid. (Fuchs.) When a solution of the salt in hydrochloric acid is mixed with tartaric acid, then with ammonia and hydrochlorate of magnesia, the whole of the phosphoric acid is precipitated in the form of phosphate of magnesia and ammonia, whilst all the alumina remains in solution. (Otto.)—The salt is insoluble in water, but dissolves in aqueous hydrochloric or nitric acid: from a solution in the latter, when neutral, acetate of lead separates a portion of the phosphoric acid as phosphate of lead. (Fuchs, *Schw.* 24, 122.) Nitrate of silver, on careful addition of ammonia, throws down yellow triphosphate of silver. (H. Rose.)

*c. Sesquiphosphate?*—Ordinary diphosphate of soda produces in a solution of alum a gelatinous precipitate, which dries up to a white tasteless powder, insoluble in water and solution of sal-ammoniac, but dissolved by acids (including acetic acid, *Wittstein*), and by caustic potash: when strongly heated, it yields a white enamel.

*d. Acid phosphate.*—Prepared by dissolving *a*, *b*, or *c* in phosphoric acid.—Leaves a gummy residue on evaporation; fuses to a clear glass; deliquesces in the air. (Fourcroy.)

PYROPHOSPHATE OF ALUMINA. ¶—Prepared by precipitating an aqueous solution of sesquichloride of aluminum with pyrophosphate of soda:

$$2Al^2Cl^3 + 3(2NaO, PO^5) = 2(Al^2O^3), 3PO^5 + 6NaCl.$$

Amorphous, white precipitate, resembling the ordinary hydrate of alumina, soluble in mineral acids and solution of pyrophosphate of soda, but not in acetic acid (which distinguishes it from the ordinary sesquiphosphate, Wittstein, *Repert.* 63, 224). The solution in sulphurous acid water is precipitated in an amorphous state by boiling. Neutral pyrophosphate of alumina is soluble in ammonia and potash; but the salt, when dissolved in hydrochloric acid and precipitated by ammonia, is not re-dissolved by excess of the reagent; a portion of phosphoric acid however remains in the solution. The hydrated salt contains 10 equivalents of water. (Schwarzenberg, *Ann. Pharm.* 65, 2.)

| | Calculation. | | Schwarzenberg. |
|---|---|---|---|
| $2Al^2O^3$ | 102·8 | 32·43 | 32·52 |
| $3PO^5$ | 214·2 | 67·57 | 67·48 |
| $2Al^2O^3, 3PO^5$ | 317·0 | 100·00 | 100·00 |

METAPHOSPHATE OF ALUMINA.—Maddrell (*Mem. Chim. Soc.* 3, 273) prepares this salt by dissolving hydrate of alumina in excess of aqueous phosphoric acid, evaporating to dryness, and heating the residue to 316°. White, anhydrous salt, insoluble in water and concentrated acids.

| | Calculation. | | Maddrell. |
|---|---|---|---|
| $Al^2O^3$ | 51·4 | 19·352 | 19·392 |
| $3PO^5$ | 214·2 | 80·648 | 80.607 |
| $Al^2O^3, 3PO^5$ | 265·6 | 100·000 | 99·999 |

## ALUMINUM AND SULPHUR.

A. SULPHIDE OF ALUMINUM.—Sulphur may be distilled over aluminum without combining with it; but when thrown upon ignited aluminum, it is absorbed with vivid incandescence. The sulphide is a black, vitrefied mass, having a semi-metallic lustre, and assuming an iron-grey colour under the burnisher. It has a pungent taste like that of hydrosulphuric acid. When exposed to the air, it gradually swells up, emitting hydrosulphuric acid, and crumbling to a greyish-white powder. Under water, it is quickly resolved into hydrosulphuric acid and greyish-coloured alumina. (Wöhler.)

B. SULPHITE OF ALUMINA. *a. Monosulphite.*—An aqueous solution of sulphurous acid is saturated, at ordinary temperatures, with hydrate of alumina, and the clear liquid heated to a temperature of 74° (165° F.), by which means the earth is precipitated and sulphurous acid gas evolved. (Gouginsperg, *Ann. Pharm.* 45, 132.)—White powder, having an earthy, sulphurous taste. (Fourcroy & Vauquelin.)—It evolves sulphurous acid, even at 100°, and when ignited for a short time, leaves a residue of alumin-

containing sulphuric acid (Fourcroy & Vauquelin); but after prolonged ignition at high temperatures, nothing but pure alumina is left behind. (Gougginsperg.) It oxidizes in the air, forming sulphate of alumina (F. & V.): hence, when in contact with water, it quickly gives up sulphate of alumina to that liquid. (Gougginsperg.)—It does not dissolve in pure water, but is soluble in an aqueous solution of sulphurous acid. (Fourcroy & Vauquelin.)

| | Calculation. | | Gougginsperg. | Fourcroy & Vauquelin. |
|---|---|---|---|---|
| $Al^2O^3$ | 51·4 | 43·05 | 43·10 | 44 |
| $SO^2$ | 32·0 | 26·79 | 27·04 | 32 |
| 4HO | 36·0 | 30·16 | 29·86 | 24 |
| $Al^2O^3, SO^2 + 4Aq.$ | 119·4 | 100·00 | 100·00 | 100 |

*b. Tersulphite?*—The solution of hydrate of alumina in aqueous sulphurous acid leaves a gummy mass when evaporated in vacuo. It gradually becomes oxidized in the air, and forms sulphate of alumina. Even at 74° (165·2° F.), it deposits all the alumina in the form of salt a, and gives off a large quantity of sulphurous acid; and the filtrate, although still containing sulphurous acid, is quite free from alumina. (*Vid.* Berthier, *Ann. Chim. Phys.* 50, 371.)

C. Hyposulphate of Alumina.—Tersulphate of alumina is precipitated by hyposulphate of baryta, the liquid filtered, and left to evaporate in the air; the salt is then deposited in very small crystals. If the evaporation is carried on to dryness, in vacuo and at ordinary temperatures, the salt soon begins to decompose, and the white amorphous mass which remains is found to contain a large quantity of sulphuric acid. (Heeren.)

D. Sulphate of Alumina.—*a. Two-fifths Sulphate?—Pissophane* consists of $5Al^2O^3, 2SO^3 + 30Aq$. A portion of the alumina is however replaced by sesquioxide of iron. (Erdmann, *Schw.* 62, 104.)

*b. Monosulphate.*—Found native as *Aluminite.*—Precipitated from an aqueous solution of tersulphate of alumina by ammonia; after washing and drying, it forms a white powder. (Berzelius.) Aluminite is a white, opaque, earthy mass, soft and coherent, of specific gravity 1·705, soluble in hydrochloric acid, and parting with all its acid at a red heat. (Stromeyer, *Schw.* 19, 424.)

| | *Aluminite.* | | Stromeyer. | Bucholz. | Simon. |
|---|---|---|---|---|---|
| $Al^2O^3$ | 51·4 | 29·81 | 29·87 | 31·0 | 32·50 |
| $SO^3$ | 40·0 | 23·20 | 23·37 | 21·5 | 19·25 |
| 9HO | 81·0 | 46·99 | 46·76 | 45·0 | 47·00 |
| Lime, silica, sesquioxide of Iron | | | | 2·0 | 1·25 |
| | 172·4 | 100·00 | 100·00 | 99·5 | 100·00 |

*c. Four-thirds Sulphate?*—This salt was found deposited in the form of a crust on the sides of a glass vessel in which dilute sulphuric acid perfectly saturated with hydrate of alumina had been kept for several years. Under the microscope, it appeared to consist of a mass of very small, transparent needles. When gently heated, it evolved water; and on ignition, sulphuric acid was given off. It was soluble in 144 parts of cold water, in 30·8 parts of boiling water, and dissolved with ease in hydrochloric or nitric acid. (Rammelsberg, *Pogg.* 43, 583.)

| | Calculation. | | Rammelsberg. |
|---|---|---|---|
| $3Al^2O^3$ | 154·2 | 26·39 | 26·67 |
| $4SO^3$ | 160·0 | 27·39 | 27·47 |
| 30HO | 270·0 | 46·22 | 45·86 |
| | 584·2 | 100·00 | 100·00 |

When moderately dilute sulphuric acid is saturated by digestion with hydrate of alumina and filtered, a liquid is obtained (according to Phillips, *Ann. Phil.* 20, 280), which, on being mixed with water, becomes turbid, and continues for many months to deposit a basic salt. This salt, after drying, is partly opaque, partly translucent like horn, and contains, besides water, 162·9 parts (rather more than 4 At.) of sulphuric acid combined with 154·2 parts (3 At.) of alumina. The liquid filtered from this precipitate has nearly the same composition, and is characterized by becoming turbid as often as it is heated, an appearance which Gay-Lussac (*Ann. Chim. Phys.* 21, 223) attributed to the presence of a foreign salt.

*d. Bisulphate.*—A concentrated solution of tersulphate of alumina is warmed for a considerable time with monosulphate; filtered hot; evaporated to dryness at a gentle heat; and the gummy mass which remains, preserved in well-closed vessels. In moist air, this salt is decomposed and becomes opaque; and in contact with water, it is resolved into tersulphate which dissolves, and monosulphate which remains behind. Also by digesting a solution of the tersulphate with carbonate of lime, a liquid is obtained, which is rendered opaque, either by boiling or by dilution with water; but contains, in addition to the bisulphate formed, a portion of tersulphate of alumina still undecomposed. (Maus, *Pogg.* 11, 80.) The same salt (contaminated with 3 per cent. of sulphate of iron and containing water) is found on Mount Ararat. (Göbel, *Schw.* 60, 401.)

| | Calculation. | | Maus. *Artif.* | Göbel. *Native.* |
|---|---|---|---|---|
| $Al^2O^3$ | 51·4 | 39·12 | 39·4 | 39·81 |
| $2SO^3$ | 80·0 | 60·88 | 60·6 | 60·19 |
| $Al^2O^3, 2SO^3$ | 131·4 | 100·00 | 100·0 | 100·00 |

In both analyses, the combined water was disregarded.

*e. Tersulphate.*—The anhydrous salt obtained by heating the crystallized salt is a spongy mass, of specific gravity 2·74 (Karsten); it parts with its acid at a red heat without fusing, and, according to Wöhler, leaves pure alumina when ignited in a current of hydrogen gas.

*With 18 atoms of water.*—Found native, composing many of the so-called *Capillary Salts* (*Haar-salze*). Prepared on the large scale, contaminated with a small quantity of alum, for manufacturing purposes. (Mohr, *Ann. Pharm.* 34, 345.) Hydrate of alumina is dissolved in dilute sulphuric acid—or, according to Descotils, ammonia alum is boiled with aqua regia till all the ammonia is destroyed—and the liquid evaporated till it acquires a syrupy consistence.—The native salt is crystalline and granular, or has a parallel fibrous structure; the artificially prepared salt exhibits thin, pearly, soft needles and laminæ. From a solution in hydrochloric acid it crystallizes in beautiful tabular crystals. (Kane.) The salt is permanent in the air, and has a rough and highly acid taste; when heated, it swells up very strongly and loses its water of crystallization; it is soluble in 2 parts of cold water, but scarcely at all in alcohol. (Berzelius.)

| | Calculation. | | Boussingault. *From Pasto.* | Rammelsberg. *From Bilin.* |
|---|---|---|---|---|
| $AlO^3$ | 51·4 | 15·42 | 14·98 | 15·86 |
| $3SO^3$ | 120·0 | 35·99 | 35·68 | 35·31 |
| 18HO | 162·0 | 48·59 | 49·34 | 48·83 |
| | 333·4 | 100·00 | 100·00 | 100·00 |

[For accounts of the native salt, *vid.* Boussingault (*Ann. Chim. Phys.* 30, 109; 52, 348); H. Rose (*Pogg.* 27, 317); Mill (*N. Quart. J. of Sc.* 3, 382); Rammelsberg (*Pogg.* 43, 130 and 399).]

## Aluminum and Selenium.

A. Selenide of Aluminum.—Aluminum heated to redness with selenium becomes incandescent and unites with the selenium, forming a black powder, which acquires a dark metallic lustre by pressure; emits an odour of seleniuretted hydrogen when exposed to the air; and rapidly evolves that gas when immersed in water, the water soon becoming red from separation of selenium.

B. Hydroselenite of Alumina.—An aqueous solution of hydroselenite of potash produces with the salts of alumina a flesh-coloured precipitate, which gives off selenium at a red heat. (Berzelius.)

C. Selenite of Alumina.—*a. Terselenite.*—Precipitated on adding selenite of potash to a perfectly neutral solution of chloride of aluminum or of alum. White powder, losing, when ignited, first water, and then the whole of its acid;—insoluble in water.

| | Calculation. | | Muspratt. |
|---|---|---|---|
| $Al^2O^3$ | 52 | 21·17 | |
| $3SeO^2$ | 168 | 68·01 | |
| 3HO | 27 | 10·82 | 10·71 |
| $Al^2O^3, 3SeO^2 + 3Aq.$ | 247 | 100·00 | |

*b. Sex-selenite.*—By dissolving the salt *a*, or the hydrate of alumina in aqueous solution of selenious acid, and evaporating. Colourless, transparent, gummy mass, having a rough taste, and easily soluble in water. (Berzelius.)

D. Ter-seleniate of Alumina.—Similar in its behaviour to the sulphuric acid salt, and yielding, under the same circumstances, corresponding basic-salts. (Berzelius, *Lehrb.* 4, 341.)

Aluminum is not affected by ignition in vapour of iodine. (Wöhler.)

## Aluminum and Bromine.

A. Bromide of Aluminum.—Bromine vapour passed over an ignited mixture of alumina and charcoal, forms bromide of aluminum; water dissolves out hydrobromate of alumina. (Löwig.)

*Hydrated Bromide of Aluminum* or *Hydrobromate of Alumina.*—A solution of hydrate of alumina in aqueous hydrobromic acid yields a

mass of needles crystallized together in tufts. The salt has a styptic taste; reddens litmus feebly; highly deliquescent; resolved by heat into hydrobromic acid gas and alumina; very soluble in water and alcohol. (Löwig, Berthemot, *Ann. Chim. Phys.* 44, 394.)

B. Bromate of Alumina.—A solution of the hydrate in the aqueous acid, concentrated under the evaporating receiver, leaves a tough, transparent mass which contains no crystals, and when exposed to the air, deliquesces to a thin liquid. (Rammelsberg, *Pogg.* 55, 63.)

## Aluminum and Chlorine.

A. Chloride of Aluminum.—Aluminum heated to redness in a current of chlorine gas takes fire, and is converted into chloride of aluminum, which sublimes. (Wöhler.)—Dry chlorine gas is passed over alumina mixed with powdered charcoal and ignited in a porcelain tube. (Oerstedt.) —Wöhler precipitates the hydrate from a hot solution of alumina with carbonate of potash; mixes it, after being thoroughly washed and dried, with powdered charcoal, sugar, and oil, to the consistence of a thick paste; ignites this paste in a covered crucible; and introduces the carbonized mass, while still hot, into a porcelain tube. To one end of this tube is attached a chloride of calcium tube through which the chlorine passes; at the other, a small tubulated glass globe with a tube for the escape of gas. As soon as the apparatus is filled with chlorine, the porcelain tube and its contents are ignited, and the chloride of aluminum carried along by the carbonic oxide gas, condenses, partly in the form of powder in the globe, and partly as a solid mass at the extremity of the porcelain tube, which is often stopped up by it. If the hydrate, thrown down by carbonate of potash from alum, is not submitted to long continued washing, sulphate of potash remains mixed with it—and, during the ignition with charcoal and chlorine, gives rise to the formation of sulphide of potassium, and subsequently of chloride of sulphur, which mixes with the chloride of aluminum. On this account, Liebig precipitates a solution of alum free from iron by a slight excess of chloride of barium; evaporates the filtrate to the thickness of syrup—from which, on cooling, the chlorides of potassium and of barium crystallize out completely; decants the solution from the crystals; mixes it with pounded sugar or starch, amounting to one-fifth of the weight of the alum employed; and ignites the whole in a covered crucible: by this process, an intimate mixture of pure alumina and charcoal is obtained. This mixture is introduced into a tube of hard glass from 2 to 2½ feet long and 6 lines in diameter, one end of which is connected by means of a cork with a tubulated receiver fitted with an open piece of barometer tube, to allow the carbonic oxide gas to escape. As the chlorine must be perfectly dry, Liebig passes it from the generator through a Woulfe's bottle containing oil of vitriol, by which means also, by observing the rapidity with which the bubbles of gas succeed each other, the rate of evolution of the chlorine may be observed and regulated. As soon as the air is entirely expelled by the chlorine, the tube is heated to redness; and when all appearance of moisture has ceased, the receiver is attached to the tube. A small quantity of the chloride of aluminum collects in the receiver in the form of a light, bulky powder; the greater portion however condenses in the cold extremity of the tube in transparent, dark-yellow drops, which solidify in a crystalline mass.

At the end of the operation, this mass is detached from the tube by means of a strong iron wire, and, together with the finely divided chloride in the receiver, put into a small retort and purified by distillation; the sublimed chloride deposits itself in the neck of the retort. (Liebig.) Pale greenish yellow (Wöhler); lemon-coloured, waxy mass (Liebig); transparent, and of a crystalline texture, resembling talc. Melts when heated under rock-oil, without however dissolving, and forms a brownish-red liquid. (Wöhler.) Fusible in large masses; a small quantity immediately evaporates on the application of heat; boils at 180°—185° (356°—365° F.). (Liebig.) Fumes slightly in the air and smells of hydrochloric acid. (Wöhler.) Decomposed by potassium at a temperature much below redness, the action being attended with brilliant incandescence and projection of part of the ingredients. Heated with potassium under rock-oil, no reaction takes place. (Wöhler.) By distilling chloride of aluminum with anhydrous sulphuric acid, sulphurous acid and chlorine are set free, and sulphate of alumina is left behind. (H. Rose.)

$$Al^2Cl^3 + 6SO^3 = Al^2O^3, 3SO^3 + 3SO^2 + 3Cl.$$

| | | Calculation. | |
|---|---|---|---|
| 2Al ..... | 27·4 | ..... | 20·51 |
| 3Cl ..... | 106·2 | ..... | 79·49 |
| $Al^2Cl^3$ ..... | 133·6 | ..... | 100·00 |

*Hydrated Chloride of Aluminum* or *Ter-hydrochlorate of Alumina.*—Chloride of aluminum rapidly deliquesces in the air, forming transparent drops, and dissolves in water with a hissing noise and evolution of heat; the solution is transparent. (Wöhler.)—A similar solution is obtained by saturating hydrochloric acid with hydrate of alumina. The solution left to evaporate in a warm and very dry atmosphere, yields regular six-sided prisms with the terminal faces of a rhombohedron, the angles of which measure about 138° (*Fig.* 146). The crystals do not effloresce in the evaporating receiver over oil of vitriol. They do not melt when heated, but evolve water and hydrochloric acid, leaving 21·605 per cent. of alumina in the form of the crystal. In an ordinary atmosphere, they deliquesce with great rapidity. (Bonsdorff, *Pogg.* 27, 279.) The salt is very soluble in water and alcohol.

| | Crystallized. | | Or: | | | | Bonsdorff. |
|---|---|---|---|---|---|---|---|
| 2Al..... | 27·4 | 11·34 | $Al^2O^3$.... | 51·4 | .... | 21·27 | .... 21·605 |
| 3Cl..... | 106·2 | 43·96 | 3HCl.... | 109·2 | .... | 45·20 | |
| 12HO ..... | 108·0 | 44·70 | 9HO .... | 81·0 | .... | 33·53 | |
| $Al^2Cl^3$ + 12Aq.... | 241·6 | 100·00 | | 241·6 | .... | 100·00 | |

B. Hydrated Chloride of Aluminum and Alumina, or Basic Hydrochlorate of Alumina.—When an aqueous solution of chloride of aluminum is mixed with a quantity of ammonia not sufficient to saturate it completely, a precipitate is formed, which, when thrown on a filter and washed, gradually becomes translucent, partially dissolves in the water, and stops up the pores of the filter. Ammonia decomposes the salt and separates hydrate of alumina. (Berzelius.)

Hydrate of alumina does not dissolve in water through which chlorine is passed. (Grouvelle.) According to Chenevix, however, it does dissolve.

C. Chlorate of Alumina.—A solution of the double fluoride of *silicium* and aluminum is precipitated with a boiling saturated solution

of chlorate of potash in equivalent proportions, then filtered, and evaporated to a small bulk.—It detonates very slightly on ignited charcoal, producing a violet-coloured flame;—deliquescent. (Berzelius.)

D. Perchlorate of Alumina.—Perchloric acid saturated with hydrate of alumina yields, on evaporation, an uncrystallizable salt which reddens litmus, deliquesces in the air, and is soluble in alcohol. (Serullas, *Ann. Chim. Phys.* 46, 304.)

E. Phosphuretted Hydrogen with Chloride of Aluminum.—Chloride of aluminum absorbs phosphuretted hydrogen gas but very slowly in the cold; after five hours, the compound contains only 3·67 per cent. of phosphuretted hydrogen. If, however, it be subsequently heated in a rapid current of the same gas till it gradually sublimes, the phosphuretted hydrogen is absorbed more abundantly, without decomposition, and the compound sublimes completely and is deposited in crystals. —These crystals dissolve in water with evolution of non-spontaneously inflammable phosphuretted hydrogen, and yield a solution of chloride of aluminum. When larger quantities are used, spontaneously inflammable gas is likewise evolved: ammonia liberates only the latter. (H. Rose, *Pogg.* 24, 295.)

| | Crystallized. | | | | H. Rose. |
|---|---|---|---|---|---|
| $3Al^2Cl^3$ | 400·8 | .... | 92·09 | .... | 91·29 |
| $PH^3$ | 34·4 | .... | 7·91 | .... | 8·71 |
| $PH^3, 3Al^2Cl^3$ | 435·2 | .... | 100·00 | .... | 100·00 |

F. Hydrosulphate of Chloride of Aluminum.—Chloride of aluminum has no action upon hydrosulphuric acid gas at ordinary temperatures.—To form the compound, chloride of aluminum is sublimed in a small retort, while a rapid current of dry hydrosulphuric acid is passed through the tubular opening: the excess of that gas is afterwards expelled by a current of dry hydrogen. The compound sublimes in the neck of the retort, partly in transparent, pearly crystals, partly in the form of a dense brittle mass, which becomes white after fusion.—Sublimes in a glass tube; it evolves a portion of the hydrosulphuric acid amounting to about 30 or 40 times its own volume. In water it is converted, with considerable rise of temperature and evolution of hydrosulphuric acid, into a solution of chloride of aluminum, rendered turbid by the presence of sulphur. It deliquesces rapidly in the air, with continued exhalation of hydrosulphuric acid. With ammonia, it yields hydrochlorate and hydrosulphate of ammonia, while hydrate of alumina is separated. (Wöhler.)

## Aluminum and Fluorine.

A. Hydrated fluoride of Aluminum or Ter-hydrofluate of Alumina.—A solution of hydrate of alumina in aqueous hydrofluoric acid yields, on evaporation, first a syrup, and subsequently a transparent, fibrous, gummy mass, easily detached from the vessel by water. By ignition it is converted into salt B, with loss of hydrofluoric acid. It is tasteless, and dissolves slowly in cold, but more rapidly in hot water. The solution attacks the glass vessel containing it. The salt forms double salts with the fluorides of zinc, nickel, and copper. (Berzelius, *Pogg.* 1, 23.)

B. Fluoride of Aluminum with Alumina.—Remains in the anhydrous state on *igniting A*, and is not further decomposed at a higher

temperature. Obtained as a hydrate, or as *basic hydrofluate of alumina*, by digesting an aqueous solution of A with hydrate of alumina: it forms a transparent jelly, which dries up to a yellowish, gummy mass. (Berzelius.)

C. Hydrated Fluoboride of Aluminum, or Hydrofluate of Borate of Alumina.—Crystallizes by slow evaporation from a solution in excess of acid. Soluble only in water which contains free acid. (Berzelius.)

On mixing the hydrofluate of borate of soda with chloride of aluminum, a basic compound separates, and the liquid contains free acid, which retains a portion of the precipitate in solution. The precipitate fuses at a red heat, evolving water and hydrofluate of boracic acid, and leaving fused borate of alumina. (Berzelius.)

## Aluminum and Nitrogen.

A. Nitrate of Alumina. *a. Basic Nitrate.*—Separates as a pasty mass when the salt *b* is decomposed by ammonia, even though the ammonia may be in excess. (Berzelius.)

*b. Ternitrate.* Prepared by saturating nitric acid with hydrate of alumina. Crystallizes, but with difficulty, in thin colourless laminæ, and generally remains in the form of a tenacious gummy mass, when the solution is evaporated. It has a rough acid taste, and reddens litmus. According to Bucholz, it contains 22 per cent. of the earth combined with 78 of acid, which is easily expelled by heat.—Very soluble in water and alcohol; deliquesces in the air.—From a solution of alumina in excess of nitric acid, the greater part of the alumina separates in flakes, slowly at ordinary temperatures, but more rapidly on the application of heat. After washing, it dries up to a granular powder, partially soluble and in small quantity only in boiling sulphuric, hydrochloric, or nitric acids. (Hollunder, *Kastn. Arch.* 12, 424.)

B. Aluminate of Ammonia.—Hydrate of alumina dissolves very sparingly in solution of ammonia. It separates again, however, after standing for some time out of contact of air. [The best precipitant for alumina in analysis is sulphide of ammonium. (Malaguti & Durocher, *N. Ann. Chim. Phys.* 16, 421.)]

C. Carbonate of Alumina and Ammonia.—*a.* When sulphate of alumina is precipitated with excess of carbonate of ammonia, the precipitate, after being digested for some time in the solution, is found to be free from sulphuric acid, but to retain a portion of the carbonate of ammonia, which is not entirely expelled even at a temperature of 100°. (Forchhammer, *Pogg.* 35, 336.)

*b.* When a solution of alum is supersaturated with concentrated carbonate of ammonia, a small quantity of the alumina dissolves and is again thrown down on heating the liquid, but not on diluting it with water. (Gmelin.)

D. Sulphate of Alumina and Ammonia.—*Ammonia-alum.*—Found native, though rarely. (Stromeyer, *Scher.* 69, 260; Blanchet & Lecanu, *J. Pharm.* 13, 419.)—*Preparation.* Sulphate of alumina is first prepared: 1. From alum-slate, lignite containing iron-pyrites, or any other

aluminous mineral penetrated with veins of sulphide of iron. These minerals are either disintegrated by exposure to the air, or roasted, or slowly burnt; the sulphate of alumina thus formed, together with the ferrous and ferric sulphates, is extracted by digestion in water—and, if necessary, the greater part of the ferrous sulphate separated by evaporation and crystallization; and the disulphate of ferric oxide, which is formed and precipitated by exposure to the air, removed by subsidence and decantation. —Or 2. By treating clay with sulphuric acid.—A solution of sulphate of alumina having been thus obtained, it is evaporated down to a certain point, and then mixed with decomposing urine (which contains ammoniacal salts): the ammonia-alum then separates, and may be purified by repeated solution and recrystallization. If the two liquids are mixed in the cold, the salt is deposited in the form of *Alum-meal* (*Alaunmehl*).—The iron contained in the salt amounting at most to 0·001, and often only to 0·0005 of the whole—is separated by dissolving the salt once or twice in a small quantity of hot water, filtering, crystallizing, and then washing the crystals with cold water. The presence of iron in the alum is detected by supersaturating the aqueous solution with potash. The alumina dissolves, and the oxide of iron is left as an insoluble residue.

Crystallizes in combination with water in transparent colourless crystals belonging to the regular system, generally in octohedrons (*Fig.* 1, 2, 4, 5, 6, 9, and 11); specific gravity, 1·626. (Kopp.) The crystals have a conchoidal fracture; a sour-sweet, rough taste; and redden litmus.

| | Crystallized. | | | Riffault. | | Forchhammer. |
|---|---|---|---|---|---|---|
| $NH^3$ | 17·0 | .... | 3·75 | | | |
| $Al^2O^3$ | 51·4 | .... | 11·34 | 11·906 | .... | 11·24 |
| $4SO^3$ | 160·0 | .... | 35·29 | 36·042 | .... | 35·90 |
| 25HO | 225·0 | .... | 49·62 | | | |
| | 453·4 | .... | 100·00 | | | |

$(NH^4O, SO^3) + (Al^2O^3, 3SO^3) + 24Aq.$; or, according to Kane, $(HO, SO^3, HAd + 6Aq) + Al^2O^3, 3SO^3 + 18Aq.$

When heated, it loses water, swells up, and forms a porous spongy mass, sometimes called *Burnt alum*, *Alumen ustum*. After strong ignition it leaves a residue of pure alumina. Cold water dissolves it sparingly; hot water much more readily.

*Basic Ammonia-alum.*—*a.* When a cold solution of ammonia-alum is mixed with ammonia till the precipitate is no longer re-dissolved on shaking the liquid, the solution is found to contain a compound of sulphate of ammonia with bisulphate of alumina, which crystallizes with difficulty, and only in the form of a crust. The solution gradually deposits monosulphate of alumina; but on the addition of water, the precipitation is immediate. (Maus, *Pogg.* 11, 81.)

*b.* If to a boiling solution of ammonia-alum, ammonia is added by degrees, but not to complete saturation, a compound separates which contains monosulphate of alumina. (Riffault, *Ann. Chim. Phys.* 16, 359.)

| | Calculation. | | | Riffault. |
|---|---|---|---|---|
| $NH^3$ | 17·0 | .... | 4·12 | |
| $3Al^2O^3$ | 154·2 | .... | 37·41 | 37·572 |
| $4SO^3$ | 160·0 | .... | 38·82 | 38·724 |
| 9HO | 81·0 | .... | 19·65 | |
| | 412·2 | .... | 100·00 | |

$NH^4O, SO^3 + 3(Al^2O^3, SO^3) + 8Aq$.—More probable, though not so strictly in accordance with Riffault's analysis is the formula: $NH^4O, SO^3 + 3(Al^2O^3SO^3) + 9Aq$.

E. Chloride of Aluminum with Ammonia.—*a*. Dry ammoniacal gas is at first slowly absorbed by chloride of aluminum; but on a sudden, the absorption takes place with such rapidity, that the compound is liquefied by the heat evolved.—*b*. When *a* is distilled [in ammoniacal gas?] the compound *b* is produced and passes over into the receiver.—*c*. The compound *a*, distilled in a vessel full of hydrogen gas, parts with an additional quantity of ammonia and yields the compound *c*.—*a* and *b* dissolve in water, with partial separation of alumina; *c* dissolves without leaving any residue. (H. Rose, *Pogg.* 24, 298; see also Persoz, *Ann. Chim. Phys.* 44, 320.)

| | Calculation. | | Persoz. | Rose. | Rose, *b*. |
|---|---|---|---|---|---|
| $3NH^3$ | 51·0 | 27·63 | 27·8 | 24·7 | 18·22 |
| $Al^2Cl^3$ | 133·6 | 72·37 | 72·2 | 75·3 | 81·78 |
| *a* | 184·6 | 100·00 | 100·0 | 100·0 | 100·00 |

| | Rose, *c*. |
|---|---|
| $NH^3$ | 13 |
| $Al^2Cl^3$ | 87 |
| *c* | 100 |

F. Fluoride of Aluminum with Hydrofluate of Ammonia.—When hydrate of alumina is digested with hydrofluate of ammonia, part of the ammonia is expelled and a transparent jelly is formed, which dries up to a white powder, and evolves when heated, first ammonia—and then bihydrofluate of ammonia, leaving a compound of fluoride of aluminum with alumina. The salt is feebly soluble in pure water, but not in water containing ammonia or hydrofluate of ammonia, either of which precipitates it from an aqueous solution. (Berzelius, *Pogg.* 1, 45.)

## Aluminum and Potassium.

A. Aluminate of Potash.—*a*. *Anhydrous*.—Alumina ignited with hydrate or carbonate of potash, combines with the potash, forming a grey loose opaque mass, soluble in acids.

*b*. *Hydrated*.—When a boiling solution of caustic potash is saturated with hydrate of alumina, evaporated to a small bulk, and the small portion of potash which remains uncombined, dissolved out by alcohol, a compound remains, consisting of 47·87 per cent. (1 At.) of potash with 51·13 per cent. (1 At.) of alumina. (Unverdorben, *Pogg.* 7, 723.) —Fremy (*Compt. rend.* 15, 1106) obtained this compound in a crystalline form with 2 atoms of water = $KO, Al^2O^3 + 2Aq$.

*c*. *Aqueous Solution*.—Prepared by dissolving *a* or *b* in water, or by saturating a hot solution of potash with hydrate of alumina. Colourless liquid, decomposed by acids and by ammoniacal salts, with separation of pure hydrate of alumina; and by baryta-water, strontia-water, milk of lime, and lime-water, with precipitation of aluminate of baryta, strontia, or lime. (Guyton-Morveau, *Ann. Chim.* 31, 246; Bucholz, *Taschenb.* 1812, 156; Döbereiner, *Schw.* 10, 113.) The decomposition effected by lime is *not complete*. (Kuhlmann, *Ann. Pharm.* 41, 228.) When a solution of

potash is saturated with hydrate of alumina precipitated by carbonate of ammonia, the solution, even when kept in well-closed bottles, deposits after some days, pure hydrate of alumina, *γ*, 2 (III., 307); this precipitation is probably caused by the carbonic acid proceeding from a portion of adhering carbonate of ammonia. If air be admitted, a still larger quantity is precipitated, by the action of the carbonic acid contained in it. (Bonsdorff, *Pogg.* 27, 275.)

B. Carbonate of Alumina and Potash.—*a.* The precipitate obtained by adding an excess of carbonate of potash to a salt of alumina, retains—however well it may be washed—a portion of carbonate of potash in a state of intimate combination; it does not evolve carbonic acid when ignited, but dissolves with effervescence in the stronger acids. (Berzelius.)

*b.* When a saturated solution of carbonate of potash is added in large excess to a solution of alum, a portion of alumina remains dissolved. (Gmelin.) A boiling concentrated solution, more especially, dissolves alumina; hence the first few drops of chloride of aluminum added to a boiling solution of carbonate of potash give no precipitate; and on increasing the quantity till a permanent precipitate begins to appear, and then filtering, the liquid as it cools deposits voluminous flakes of hydrate of alumina: a portion however still remains dissolved after the solution has become cold, and may be thrown down by neutralizing with hydrochloric acid and then adding carbonate of ammonia. (Magnus, *Pogg.* 21, 58.)

C. Sulphate of Alumina and Potash.—*Potash-alum.* — Found native in a few minerals, and as an efflorescence.—*Preparation.*—1. The aluminous earth of volcanic regions, or alum-stone previously ignited, is exhausted with water, and the solution evaporated.—2. Sulphate of alumina is prepared as for ammonia alum (III., 319), and substances containing potash are added to it—as the ley from wood-ashes, crude potash, sulphate of potash, and chloride of potassium: hence also glass-gall, soap-boilers' ley, &c. may be used. Potash alum then crystallizes out, and may be afterwards purified by repeated crystallization. Crystalline form, fracture, taste, and other characters, similar to those of ammonia-alum. Specific gravity = 1·724. (Kopp.)

| | Crystallized. | | Thomson. | Thénard & Roard. | Vauquelin. | Graham. |
|---|---|---|---|---|---|---|
| KO | 47·2 | 9·95 | 9·86 | 10·02 | 10·40 | |
| $Al^2O^3$ | 51·4 | 10·83 | 11·09 | 12·53 | 10·50 | 54·11 |
| $4SO^3$ | 160·0 | 33·71 | 32·85 | 26·04 | 30·52 | |
| 24HO | 216·0 | 45·51 | 46·20 | 51·41 | 48·58 | 45·89 |
| Potash-alum. | 474·6 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

According to Kane: $(KO,SO^3+6Aq.)+(Al^2O^3,3SO^3+18Aq.)$; according to Graham: $KO,SO^3+(Al^2O^3,3SO^3+6Aq.+18Aq.)$.

Crystallized alum loses 18 atoms of water at 61° (Graham, *Ann. Pharm.* 26, 30); at 92°, it fuses completely in its own water of crystallization; and then, according to Marx (*J. pr. Chem.* 22, 143), remains liquid for some time after cooling, and finally solidifies in a crystalline mass. When gradually heated to a temperature just below redness, it loses water, swells up very much, and leaves a residue of anhydrous alum (*Burnt alum, Alumen ustum*), which forms a loose, friable, porous mass. At a white heat, the whole of the sulphuric acid which was in combination with *the alumina is* given off, partly undecomposed, as anhydrous

acid, and partly resolved into sulphurous acid and oxygen gases; leaving a mixture of alumina and sulphate of potash. When the crystals are heated in a retort, an aqueous solution of sulphurous acid collects in the receiver (*Spirit of alum*). By ignition with charcoal, potash-alum is converted into a pyrophosphorus.

Crystallized alum heated with chloride of potassium or chloride of sodium, liberates hydrochloric acid. When a concentrated solution is boiled with chloride of potassium, hydrochloric acid is evolved, and a very sparingly soluble basic-alum is precipitated; with chloride of sodium, a still more difficultly soluble salt is thrown down; and with sal-ammoniac, an alum which is almost wholly insoluble in water. A solution of alum, common salt, and nitre dissolves gold. (Richter, *Stöchiometrie*, 2, 269 and 276.) Burnt alum exposed to the air in summer, absorbs 18 atoms of water in 47 days, and the absorption does not cease even then. (Blücher.)

Crystallized alum fused at 100° and kept at this temperature for a long time, loses water, amounting in the whole to 18·95 per cent.—and becomes more and more viscid, till at last it solidifies to a clear, vitreous mass containing only 14 atoms of water.—At a temperature of 120° (248° F.) this mass swells up and loses water; and if kept at that temperature for 12 hours, till it sustains no further loss of weight, it gives off water amounting to 36·094 parts (in 100 parts of crystallized alum) —and is converted into a porous mass, which contains 5 atoms of water, and undergoes no further change at any temperature below 160° (320° F.). At 180° (356° F.) the total loss of water amounts to 43·505 per cent.; consequently, the residue contains only one atom, or 3·452 per cent.; and at 280° (536° F.) it reaches 44·439 per cent., so that the residue retains but ½ At. or 1·836 per cent. (Hertwig, *Pogg.* 55, 99.) ¶ According to Gerhardt (*J. Pharm.* 12, 57), crystallized alum loses 20 atoms of water at 120°; the residue is readily soluble in water. At 200° the whole of the water is expelled, and the remaining compound is insoluble in water. A similar result is obtained on treating the crystals with concentrated sulphuric acid and applying heat, the crystals after a short time crumbling to an insoluble powder. This powder changes under water, in the course of 8 or 10 days, into small octohedrons. ¶

Large crystals of alum kept under cold oil of vitriol for a fortnight, break up into a white pasty mass, which, when exposed to the air, absorbs water and forms octohedral crystals. On the addition of a small quantity of water, the mass becomes heated and solidifies; and if it be then dissolved in boiling water, it yields, on cooling, regular octohedrons which contain only 31·741 per cent. (14 atoms) of water, corresponding therefore in amount of water to the mass obtained by heating alum to 100°. (Hertwig.) The crystals obtained in this manner consist of ordinary alum, with 46·3 per cent. (24 atoms) of water. (W. Heintz, *Pogg.* 55, 331.)—Powdered alum rubbed up with oil of vitriol becomes heated and forms a paste which solidifies on cooling. Melted at 70° or 80° and then cooled, the mass suddenly becomes solid at 40°, the thermometer rising to 60°. The fused mass heated to 130°, boils up and gives off vapour of water; at 140° it thickens and deposits a crystalline powder, the quantity of which is increased by addition of oil of vitriol. This powder, after being washed upon a filter and then dried, contains 9·4 per cent. (3 atoms) of water, which escapes even at a temperature of 100°. It dissolves very slowly in cold water, and in about 20 minutes in boiling water. (Hertwig.) [It has not yet been determined whether the potash, alumina, and sulphuric acid in this salt are in the same proportions as in alum.]

One part of crystallized potash-alum dissolves at 12·5° (54·5° F.) in 13·3 parts of water; at 21° (69·8° F.), in 8·2 pts.; at 25° (77° F.), in 4·5 pts.; at 37·5° (99·5° F.), in 2·2 pts.; at 50° (122° F.), in 2 pts.; at 62·5° (144·5° F.), in 0·4 pts.; at 75° (167° F.), in 0·1 pt.; and at 87·5° (189·5° F.), in 0·06 pt. of water. (Brandes.) Specific gravity of a saturated solution at 8° (46·4° F.) = 1·045. (Anthon.) [For tables of the amount per cent. contained in a solution, see Richter, *Stöchiometrie*, 3, 183.] Burnt alum takes a long time to dissolve in water. Alum thrown into water immediately after it has been burned and become cool, remains almost entirely undissolved after many months; but if it has been previously exposed to the air for a fortnight, it regains its peculiar taste and dissolves with ease. (Geiger, *Mag. Pharm.* 8, 199.) In an aqueous solution of tersulphate of alumina, alum is nearly insoluble.

*Cubic Alum.*—12 parts of alum dissolved in boiling water with one part of slaked lime, yield cubical crystals on cooling. (Sieffert, *Taschenb.* 1780, 6.) A slight addition of potash to a solution of alum likewise causes the formation of cubic alum. According to Berzelius, a tolerably large quantity of potash may be added to a solution of alum before a permanent precipitate is formed.

*Basic Potash-alum.*—*a.* Containing *Bisulphate of Alumina.*—Prepared in the same manner as basic ammonia-alum, *a* (III., 319). (Maus.)

*b.* Containing *Monosulphate of Alumina.*—Found native as *Alum-stone.* (Cordier, *Schw.* 33, 282.)—1. Hydrate of alumina boiled with a solution of alum withdraws the water from the alum, and forms an insoluble powder.—2. By precipitating a boiling solution of alum with a quantity of potash insufficient for complete saturation. (Riffault, *Ann. Chim. Phys.* 16, 355; also *Schw.* 32, 450.)—Alum-stone crystallizes in acute rhombohedrons (*Fig.* 151 and 153). $r^3 : r^5 = 87° 8'$; $r^1 : r^3$ or $r^5 = 92° 52'$; cleavage parallel to $p$; specific gravity = 2·694. Translucent; infusible in the blowpipe-flame. Insoluble in water; but, after gentle ignition, gives up alum to it, the excess of alumina remaining undissolved. The artificial compound is a white, tasteless powder, which is insoluble in water, and after solution in acids, again yields crystals of alum.

| | Calculation. | | Riffault. *Artif.* 2. | Cordier. *Cryst. Alumstone.* | Descotils. *Alumstone.* |
|---|---|---|---|---|---|
| KO | 47·2 | 10·62 | 10·82 | 10·02 | 13·8 |
| $3AlO^3$ | 156·2 | 35·15 | 35·17 | 39·65 | 40·0 |
| $4SO^3$ | 160·0 | 36·00 | 36·19 | 35·50 | 35·6 |
| 9HO | 81·0 | 18·23 | 17·82 | 14·83 | 10·6 |
| | 444·4 | 100·00 | 100·00 | 100·00 | 100·0 |

$KO,SO^3+3Al^2O^3,3SO^3+9Aq.$; the analysis of Cordier however corresponds more nearly to the formula: $KO,SO^3+4Al^2O^3,3SO^3+8Aq.$, and that of Collet-Descotils to the formula: $KO,SO^3+3Al^2O^3,2SO^3+4Aq.$

*Mixture of Potash-alum and Ammonia-alum.*—Obtained by mixing solutions which contain sulphate of alumina with substances in which both ammonia and potash are present at the same time.—Corresponds exactly in appearance with potash and ammonia-alum; behaves in its chemical relations as a mere mechanical mixture of the two salts.

D. Chloride of Aluminum and Potassium.—1. In the decomposition of chloride of aluminum by potassium, there is formed, together with the aluminum, a fused mixture of the two metallic chlorides. (Wöhler.)—2. *In the preparation* of chloride of aluminum from chlorine and

alumina mixed with charcoal, if the alumina contains potash, the first volatile product is pure chloride of aluminum; but after a time, colourless drops are deposited in the tube close to the carbonaceous mixture; and these solidify to a colourless, translucent mass, of crystalline texture. This substance slowly deliquesces in the air, forming a colourless liquid; dissolves readily, and with evolution of heat, in water; and, on evaporating the solution to dryness and igniting, yields 64·48 per cent. of a mixture containing 26·67 per cent. of alumina and 37·81 per cent. of chloride of potassium. (Degen, *Ann. Pharm.* 18, 332.)

| | | Calculation. |
|---|---|---|
| KCl | 74·6 | 35·83 |
| $Al^2Cl^3$ | 133·6 | 64·17 |
| KCl, $Al^2Cl^3$ | 208·2 | 100·00 |

E. Fluoride of Aluminum and Potassium.—*a.* $3KF, Al^2F^3$.—Into an aqueous solution of fluoride of potassium a solution of fluoride of aluminum is gradually dropped, till the former salt remains only in slight excess.—A permanent precipitate is produced in a solution of alum, only when excess of fluoride of potassium is added. (Berzelius.)

*b.* $2KF, Al^2F^3$.—1. An aqueous solution of fluoride of aluminum is precipitated by stirring it up with a quantity of fluoride of potassium, smaller than is necessary for perfect saturation.—2. Hydrate of alumina is digested in an aqueous solution of bi-hydrofluate of potash. The first portions of the hydrate dissolve; by adding more, however, the compound *b* is separated, while monofluoride of potassium remains dissolved.

$$3(KO,2HF) + Al^2O^3 = 2KF, Al^2F^3 + KO, HF + 5HO.$$

If, however, the gelatinous precipitate is boiled with the supernatant liquid, it combines with another equivalent of fluoride of potassium, and is converted into *a*.

$$2KF, Al^2F^3 + KO, HF = 3KF, Al^2F^3 + HO.$$

—The gelatinous precipitate resembles *a*, and is likewise decomposed by ignition.—By boiling an aqueous solution of bi-hydrofluate of potash with excess of hydrate of alumina, the compound *b* is first formed and then the compound *a*; if the solution be then boiled, potash is set free and a *basic double salt* produced.

The precipitate *a*, as well as *b*, is gelatinous, and dries up to a white powder, which is decomposed at a red heat (by the action of adhering water). When boiled with a mixture of equal parts of oil of vitriol and water, it evolves the whole of the hydrofluoric acid; and if ammonia be then added, a precipitate of alumina is obtained free from hydrofluoric acid and potash. (Berzelius, *Pogg.* 1, 43; 4, 130; *Lehrb.* 4, 324.)—Very sparingly dissolved by acids, and still less by water. (Gay-Lussac & Thénard.)

| | *a.* | | *b.* | | Berzelius. |
|---|---|---|---|---|---|
| 3K | 117·6 | 45·72 | 2K | 78·4 | 39·34 | 40·46 |
| 2Al | 27·4 | 10·65 | 2Al | 27·4 | 13·75 | 14·32 |
| 6F | 112·2 | 43·63 | 5F | 93·5 | 46·91 | |
| *a.* | 257·2 | 100·00 | *b.* | 199·3 | 100·00 | |

## Aluminum and Sodium.

A. Aluminate of Soda.—*a. Anhydrous.*—51·4 parts (one At.) of alumina fused with excess of carbonate of soda, rapidly expel 22·6 parts (rather more than one atom) of carbonic acid.—The fused aluminate of soda is a white enamel, having a conchoidal fracture, and very fusible. It dissolves easily and completely in cold water, and when exposed to the air becomes covered with an efflorescence of carbonate of soda. (Count Schaffgotsch, *Pogg.* 43, 117.)—Before the blowpipe, alumina swells up with carbonate of soda and combines with a portion of it, but does not fuse, the excess of carbonate of soda sinking into the charcoal. (Berzelius.)

| | Calculation. | | Schaffgotsch. |
|---|---|---|---|
| $NaO$ | 31·2 | 37·77 | 38·35 |
| $Al^2O^3$ | 51·4 | 62·23 | 61·65 |
| $NaO, Al^2O^3$ | 82·6 | 100·00 | 100·00 |

*b. In solution.*—Prepared by dissolving *a* in water, or hydrate of alumina in a solution of caustic soda.—Precipitated by acids, even by the carbonic acid in the air, and by ammoniacal salts.

B. One part of *alumina* yields, by ignition with 2 parts of *borax*, a light grey, perfectly transparent glass. (Morveau.)—Before the blowpipe, alumina slowly dissolves in borax, forming a clear glass, which remains clear after cooling; but if the alumina is in excess, the bead is turbid even while hot, and becomes crystalline at the surface on cooling. (Berzelius.)

¶—C. Pyrophosphate of Alumina and Soda.—Colourless, very soluble salt. A solution of this compound may be evaporated to a certain extent, without suffering decomposition; but if the concentration be carried further, pyrophosphate of alumina is deposited, and a second double salt with excess of base produced. (J. Persoz, *Ann. Pharm.* 65, 163, 1848.) ¶

D. Alumina heated in the blowpipe-flame with microcosmic salt in any proportions whatever, forms a permanently transparent glass; an excess of alumina remains undissolved and becomes translucent. (Berzelius.)

E. Sulphate of Alumina and Soda.—*Soda-alum.*—A natural product. (Shepard, *Sillim. Amer. J.* 16, 203; Th. Thomson.) Crystallizes from the mother-liquor of alum, when soap-boiler's ley (which contains common salt) has been used in its preparation. (Zellner.)—Prepared by spontaneous evaporation of a mixed solution of sulphate of soda and tersulphate of alumina. (Zellner.)—Octohedrons, perfectly resembling potash-alum in appearance (Zellner, *Schw.* 18, 344), but having their faces hollowed out here and there with hexagonal, step-like indentations (Wellner, *Gilb.* 70, 185); specific gravity 1·6; very friable. (Ure, *Schw.* 36, 183.)

| | Crystallized. | | Wellner. | Ure. | Zellner. | Graham. |
|---|---|---|---|---|---|---|
| $NaO$ | 31·2 | 6·80 | 6·29 | 6·48 | 6·67 | |
| $Al^2O^3$ | 51·4 | 11·21 | 10·19 | 10·75 | 11·00 | 52·53 |
| $4SO^3$ | 160·0 | 34·89 | 35·10 | 34·00 | 34·32 | |
| $24HO$ | 216·0 | 47·10 | 48·22 | 49·00 | 48·01 | 47·47 |
| | 458·6 | 100·00 | 99·80 | 100·23 | 100·00 | 100·00 |

The crystals effloresce only in dry air (Graham); at temperatures between 40° and 50° they become opaque and part with their water of crystallization, without however losing their form (Zellner); they lose the whole of their water at a red heat; the residue is still perfectly soluble in water. (Ure.) They dissolve in 2·14 parts of water at 13° (55·4° F.), and in one part of boiling water; the latter solution solidifies, on cooling, to an irregular mass, not distinctly crystalline. (Zellner.) 110 parts of soda-alum dissolve in 100 parts of water at 15·5° (59·9° F.), forming a solution of specific gravity 1·296. (Ure.)—Insoluble in absolute alcohol. (Zellner.)

E. Chloride of Aluminum and Sodium.—Common salt heated with chloride of aluminum combines with it in considerable quantities, forming a yellow compound which does not give off chloride of aluminum when strongly ignited; and dissolves in water with evolution of heat, forming a solution which, on evaporation, yields crystals of pure chloride of sodium. (Wöhler.)

F. Fluoride of Aluminum and Sodium.—Found native in the form of *Kryolite*.—Prepared artificially by adding hydrate of alumina, in small portions at a time, to an aqueous solution of bi-hydrofluate of soda, till the acid reaction of the liquid—now consisting of almost pure water—disappears. The same compound is formed by acting on mono-hydrofluate of soda with alumina; only in this case, half the soda is set at liberty, and remains dissolved in the liquid.

Kryolite belongs to the square prismatic system; has a specific gravity of 2·96; is softer than fluorspar; colourless and transparent; fuses below a red heat, and forms an opaque glass on cooling. The artificially prepared salt is gelatinous while moist, and dries up to a white powder. (Berzelius, *Pogg.* 1, 41.)—Exposed to the air for a long time in a fused state, it gives off hydrofluoric acid and becomes infusible. (Smithson.) Evolves hydrofluoric acid when heated with oil of vitriol. Very slightly soluble in water. (Berzelius.)

| | Kryolite. | | | Berzelius. |
|---|---|---|---|---|
| 3Na | 69·6 | 33·27 | | 32·93 |
| 2Al | 27·4 | 13·10 | | 13·00 |
| 6F | 112·2 | 53·63 | | 54·07 |
| $3NaF, AlF^3$ | 209·2 | 100·00 | | 100·00 |

## Aluminum and Lithium.

A. Phosphate of Alumina and Lithia.—Formed when a saturated solution of phosphate of alumina in caustic potash is precipitated by a salt of lithia. (Berzelius.) ¶ A bulky precipitate is then produced, composed of $2(3LiO, PO^5) + Al^2O^3, PO^5 + 30HO$; or: $2(3LiO, PO^5) + Al^2O^3, PO^5 + 15HO + 5Al^2O^3, 3HO$. (Rammelsberg, *Pogg.* 64, 251 and 405; *Ann. Pharm.* 56, 210.) ¶ This compound is found in combination with double fluoride of aluminum and lithium, in *Amblygonite*. (Berzelius.)

B. Sulphate of Alumina and Lithia.—*Lithia-alum*.—A mixed solution of sulphate of lithia and tersulphate of alumina yields, when evaporated in the air, at temperatures below 11° (51·8° F.), octohedrons and rhombic-dodecahedrons, which are soluble in 24 parts of cold, and in 0·87 parts of hot water. (Kralovanszky, *Schw.* 54, 349.)

| | Crystallized. | | Kralovanszky. |
|---|---|---|---|
| $LO, SO^3$ | 54·4 .... 12·31 | ..... | 13·56 |
| $Al^2O^3, 3SO^3$ | 171·4 .... 38·80 | ..... | 35·83 |
| 24HO | 216·0 .... 48·89 | ..... | 50·61 |
| | 441·8 .... 100·00 | ..... | 100·00 |

According to Rammelsberg, sulphate of lithia does not form a double salt with sulphate of alumina. (*Pharm. Centr.* 1849, 106.)

C. Fluoride of Aluminum and Lithium.—Insoluble in water. (Berzelius.)

### Aluminum and Barium.

Aluminate of Baryta.—*a. Anhydrous.*—Alumina ignited with baryta yields a greenish or blue mass, having but little coherence. (Vauquelin.)

*b. Hydrated.*—By boiling baryta-water with hydrate of alumina, a soluble compound of baryta and alumina is obtained, in which the baryta predominates, and an insoluble compound in which the alumina is in excess. (Vauquelin.)—An aqueous solution of aluminate of potash ($KO, Al^2O^3$) gives with chloride of barium a gelatinous precipitate = $BaO, Al^2O^3$. (Unverdorben.)

### Aluminum and Strontium.

Aluminate of Strontia.—According to Vauquelin, alumina yields with strontia, both in the wet and in the dry way, compounds similar to those which it forms with baryta.

### Aluminum and Calcium.

Aluminate of Lime.—*a.* Alumina may be fused with from $\frac{1}{4}$ to $\frac{1}{2}$ its weight of lime; with a larger proportion of lime, no fusion takes place. (Erman, Kirwan.)—$3CaO, Al^2O^3$ is a vitreous mass, which is infusible before the blowpipe, and, after some months, crumbles to a fine powder.—$3CaO, Al^2O^3$ is sometimes of a dense, and sometimes of a porous texture, of specific gravity 2·76, and rather fusible.—$CaO, Al^2O^3$ is a compact vitrefied mass, having a waxy fracture, and very difficult of fusion. (Sefström.)

*b.* Hydrate of alumina absorbs the whole of the lime from lime-water, forming with it an insoluble compound. (Scheele.)—The same effect is produced by adding lime-water or milk of lime to an aqueous solution of aluminate of potash, pure potash remaining in the liquid. From this cause, according to Kuhlmann, lime becomes hardened in a solution of aluminate of potash or soda.—Aluminate of potash ($KO, Al^2O^3$) gives a precipitate with chloride of calcium = $CaO, Al^2O^3$. (Unverdorben.)

### Aluminum and Magnesium.

A. Aluminate of Magnesia.—*a. Anhydrous.*—*Spinelle* occurs in regular octohedrons and rhombic dodecahedrons, of specific gravity

3·48—3·62 (Breithaupt), very hard and infusible before the blowpipe. Mixed with six times its weight of carbonate of baryta and exposed to the heat of a very powerful wind-furnace, it yields a perfectly fused mass, crystalline on the surface and completely soluble in hydrochloric acid. Powdered spinelle becomes blue by ignition with nitrate of cobalt. When heated in oil of vitriol, till the latter begins to evaporate, about one-third of it dissolves; hydrochloric acid dissolves it but very slightly, and nitric acid leaves it altogether untouched. (Abich, *Pogg.* 23, 316.)

| | | *Spinelle* from Ceylon. | | | Abich. |
|---|---|---|---|---|---|
| MgO | 20·0 | | 28·01 | | 26·21 |
| $Al^2O^3$ | 51·4 | | 71·99 | | 69·01 |
| Protoxide of Iron | 0·71 | Oxide of Chromium | 1·10 | Silica 2·02 | 3·83 |
| MgO, $Al^2O^3$ | 71·4 | | 100·00 | | 99·05 |

The spinelle from Acre is entirely free from silica. (H. Rose, *Pogg.* 51, 279.)

Alumina does not fuse with magnesia, even at the heat of a smith's forge.

Alumina containing not more than one-half per cent. of magnesia evolves a considerable quantity of heat, on being moistened with water after ignition; and when treated with concentrated hydrochloric acid, leaves a powder which resists the action of the acid for a very long time. This powder is an aluminate of magnesia. (Berzelius.)

*b. Hydrated.*—When a salt of magnesia is mixed with a salt of alumina, in such proportions that the solution contains one atom of each of the bases, and chloride of aluminum is added in sufficient quantity to prevent the precipitation of the magnesia (III., 224, 225), the alumina thrown down by supersaturating with ammonia, carries with it nearly all the magnesia, producing an artificial [hydrated] spinelle. (Abich, *Pogg.* 23, 355.) An aqueous solution of potash dissolves out only a portion of the alumina from this precipitate, the rest being retained by the magnesia.

The precipitate which ammonia produces in a mixed solution of a salt of alumina and magnesia, contains, beside alumina and magnesia, a considerable quantity of ammonia, which is evolved on triturating the precipitate with potash. The precipitate produced by potash likewise appears to contain potash. (Fuchs, *Schw.* 24, 384.)

Magnesia, added to an aqueous solution of aluminate of potash, withdraws a portion of the earth, probably mixed with potash.

B. Phosphate of Alumina and Magnesia.—Occurs in the state of hydrate, forming the mineral called *Lazulite*, in which however a portion of the magnesia is replaced by protoxide of iron. Specific gravity, 3·0... 3·1; harder than apatite.—Transparent, and of a blue colour. Swells up before the blowpipe, becomes colourless, and falls to pieces without fusing; colours the flame pale bluish-green. Acids do not attack it till after ignition. Composition: $2MgO, PO^5 + 2Al^2O^3, PO^5 + 2Aq$. (Fuchs.)—¶ According to Rammelsberg (*Pogg.* 64, 251 and 405), the formula for Lazulite is $2(3RO, PO^5) + 4(Al^2O^3, 3PO^5) + 6HO$. Lazulite is distinguished from blue spar by its containing a larger quantity of protoxide of iron. ¶

C. Sulphate of Alumina and Magnesia.—*a. Magnesia-alum.*—

Found native, forming a kind of *fibrous alum.* (Stromeyer, *Schw.* 69, 255; Apjohn, *J. pr. Chem.* 13, 255.)

| | Calculation. | | Stromeyer. |
|---|---|---|---|
| MgO | 20·0 | 4·38 | 3·690 |
| $Al^2O^3$ | 51·4 | 11·26 | 11·515 |
| $4SO^3$ | 160·0 | 35·06 | 36·770 |
| 25HO | 225·0 | 49·30 | 45·739 |
| Protoxide of Manganese | | | 2·167 |
| | 456·4 | 100·00 | 99·881 |

In the native magnesia-alum, part of the magnesia is replaced by protoxide of manganese. According to Kane: $(MgO, SO^3HO) + (Al^2O^3, 3SO^3) + 24Aq.$; Kane regards MgO, HO as isomorphous with $NH^3$, HO and with KO.

*b. With a larger proportion of Sulphate of Magnesia.*—Crystallizes when a solution containing sulphate of magnesia and sulphate of alumina with a large excess of acid, is left to itself, in a porcelain basin with a rough surface. Forms a warty efflorescence composed of fine needles. (Klauer, *Ann. Pharm.* 14, 264.)

$$3(MgO, SO^3) + Al^2O^3, 3SO^3 + 36Aq.$$

| | Crystallized. | | Klauer. |
|---|---|---|---|
| 3MgO | 60·0 | 8·88 | 9·175 |
| $Al^2O^3$ | 51·4 | 7·61 | 7·600 |
| $6SO^3$ | 240·0 | 35·54 | 36·940 |
| 36HO | 324·0 | 47·97 | 46·285 |
| | 675·4 | 100·00 | 100·000 |

## Aluminum and Glucinum.

Aluminate of Glucina. — *Chrysoberyl.* — Belongs to the right prismatic system; specific gravity = 3·75 (Mohs); harder than topaz; infusible before the blowpipe; insoluble in acids.

| | *Chrysoberyl.* | | Awdejew. |
|---|---|---|---|
| GO | 12·7 | 19·81 | 18·06 |
| $Al^2O^3$ | 51·4 | 80·19 | 78·71 |
| Ferric oxide | | | 3·47 |
| GO, $Al^2O^3$ | 64·1 | 100·00 | 100·24 |

Aluminum likewise combines with *Iron.*

Chapter XIII.

# THORINUM.

Berzelius. *Pogg.* 16, 385.

*History.* Berzelius (*Schw.* 21, 25) in 1815 found in Ytterite from Kararfvet, and in the fluoride of cerium and yttro-fluoride of cerium from Finbo, a substance which he regarded as a new and peculiar earth, and named *Thoria* or *Thorina*. Subsequently, however (*Pogg.* 4, 145), he became convinced that this substance really consisted of basic phosphate of yttria. In 1828, Berzelius discovered another earth, which he proved to be distinct from all others. This he accurately investigated; and as it exhibited a great similarity to the earlier discovered substance, he conferred on it the same name. The whole of the following account, except where the contrary is stated, is taken from Berzelius.

*Sources.* As basic earth to the amount of 58 per cent. in Thorite, a mineral resembling Gadolinite, from the island of Löv-ön in Norway; also in Monazite (Kersten, *Pogg.* 47, 385), and in Pyrochlorite (Wöhler, *Pogg.* 48, 83).

*Preparation.* A mixture of potassium and double fluoride of thorinum and potassium—or, better, of potassium and chloride of thorinum (or double chloride of thorinum and potassium)—is heated in a glass tube. The act of decomposition is attended with feeble explosion. The residue consists of a grey mass, which evolves hydrogen gas only when first immersed in water, and after the fluoride or chloride of potassium has been washed out, leaves pure thorinum.

*Properties.* Dark leaden grey, heavy powder, which, when pressed in an agate mortar, assumes an iron-grey colour and metallic lustre.

## *Compounds of Thorinum.*

### Thorinum and Oxygen.

### Thorina. ThO.

*Thorinerde, Thorerde, Oxide of Thorinum, Thorine.*

*Formation.* Thorinum heated in the air to a temperature short of redness, burns with great splendour, and forms snow-white, infusible thorina. Grains of thorinum thrown into the flame of a spirit-lamp burn

with a white light, and appear at the moment of combustion to increase considerably in volume. Thorinum dissolves but very slightly in nitric acid even at a boiling heat; after long digestion, however, complete solution takes place; it is not oxidized by boiling water. It dissolves slowly in cold and rapidly in hot hydrochloric acid, with evolution of hydrogen gas. When it is immersed in dilute sulphuric acid, violent effervescence takes place at first, from disengagement of hydrogen gas; but this soon ceases, and solution then goes on very slowly till the whole has disappeared. Hence the thorina sometimes mixed with the metal may be separated by means of dilute sulphuric acid. Aqueous hydrofluoric acid behaves in a similar manner; alkaline solutions do not affect thorinum.

*Preparation.* Thorite reduced to powder but not ignited (containing thorina, potash, soda, lime, magnesia, alumina, silica, protoxide of manganese, the sesquioxides of iron and uranium, binoxide of tin, oxide of lead, and water) is warmed with hydrochloric acid. Chlorine gas is then evolved and the powder is converted into a jelly. The whole is then evaporated to dryness; the residue dissolved in water acidulated with hydrochloric acid; the tin and lead separated from the filtered solution by a current of sulphuretted hydrogen; and the thorina, together with alumina and the sesquioxides of uranium, iron, and manganese, precipitated from the filtrate by ammonia. The precipitate, after being well washed, is dissolved in dilute sulphuric acid, and the solution evaporated at a gentle heat; the sulphate of thorina is then deposited in the form of a bulky salt, difficultly soluble in the hot liquid. The supernatant liquid, after being reduced to a small bulk, is poured off—the residual salt washed with boiling water (cold would dissolve it)—pressed out—and strongly ignited: the residue is pure thorina.—The solution poured off from the sulphate of thorina still contains a portion of thorina; it is therefore concentrated by evaporation; neutralized with carbonate of potash; and mixed with a boiling saturated solution of sulphate of potash. The precipitate of sulphate of thorina and potash, with excess of sulphate of potash, which forms on cooling—is washed with water saturated with the latter salt—then dissolved in warm water—and the hydrate of thorina precipitated by ammonia. This, when ignited, yields an earth which is coloured yellow from the presence of manganese: it is purified by solution in sulphuric acid, &c., as already described. Precipitation by oxalic acid does not effect so complete a separation.

*Properties.* Snow-white; specific gravity 9·402; after ignition, it becomes hard and difficult to powder finely; infusible before the blowpipe.

| | | Calculation. | |
|---|---|---|---|
| Th | 59·6 | ..... | 88·17 |
| O | 8·0 | ..... | 11·83 |
| ThO | 67·6 | ..... | 100·00 |

(ThO = 744·9 + 100 = 844·9. Berzelius.)

Thorina is not reduced to the metallic state, either by charcoal or by potassium.

*Combinations.—a.* With water.—Hydrate of Thorina.—Sulphate of thorina, after being well purified by washing with boiling water, is dissolved in cold water, precipitated by potash, and the precipitate thoroughly

washed. The hydrate forms a gelatinous precipitate resembling hydrate of alumina, but readily sinks into a small bulk on the filter; it cakes together when dried in the air, forming hard, glassy lumps; in vacuo over oil of vitriol, it dries up to a white powder. The water is expelled by gentle ignition.

*b.* With acids, forming the SALTS OF THORINA.—The earth, after ignition, is perfectly insoluble in hydrochloric and nitric acids, but dissolves in hot sulphuric acid; the hydrate while moist is readily dissolved by acids, but with difficulty when dry. The salts of thorina are colourless, and have a pure and strongly astringent taste, without sweetness or bitterness. When heated to redness, they part with their acid on ignition (if it is volatile) more easily than the salts of zirconia. The aqueous solutions of many thorina-salts are decomposed by boiling, and deposit a white solid crust on the sides of the glass vessel. Potash or ammonia added to the solution precipitates hydrate of thorina which is not re-dissolved by an excess of the reagent; hydrosulphate of ammonia also throws down hydrate of thorina. Carbonate of ammonia or potash precipitates carbonate of thorina, soluble in excess of the alkaline carbonate at ordinary temperatures.—Phosphate of soda precipitates phosphate of thorina in white flakes.—Crystals of sulphate of potash introduced into the solution of any salt of thorina, slowly render it turbid, and give rise to the formation of double sulphate of thorina and potash, which is soluble in pure water.—Tungstic acid, alkaline molybdates and arseniates, and ferrocyanide of potassium, produce a white precipitate. Alkaline oxalates and oxalic acid also give a white precipitate, even when the thorina-salt contains a large excess of free acid.

### THORINUM AND CARBON.

CARBONATE OF THORINA.—The hydrate absorbs carbonic acid from the air while being washed and dried. When the aqueous solution of a salt of thorina is treated with alkaline carbonates, carbonic acid gas is expelled, and a basic salt precipitated which is insoluble in aqueous carbonic acid.

### THORINUM AND BORON.

BORATE OF THORINA.—Formed by double decomposition.—White, floculent precipitate, insoluble both in water and in solution of boracic acid.

### THORINUM AND PHOSPHORUS.

A. PHOSPHIDE OF THORINUM.—Heated thorinum absorbs vapour of phosphorus, the combination being attended with evolution of light and heat. The compound, which has a dark-grey colour and metallic lustre, and resembles graphite in appearance, burns when heated, and forms phosphate of thorina: it is not acted on by water.

B. PHOSPHATE OF THORINA.—White, floculent precipitate, fusing with difficulty in the blowpipe-flame; insoluble in water or in solution of phosphoric acid.

### Thorinum and Sulphur.

A. Sulphide of Thorinum.—When thorinum is mixed with sulphur, and the mixture heated till the sulphur begins to volatilize, combination takes place, and the metal burns almost as brilliantly as in the air. Yellow powder, which acquires by pressure a certain degree of lustre, but not the metallic lustre. Heated in a glass tube containing air, it gives off sulphur without much combustion, and leaves thorina. It does not undergo any change in cold aqua-regia, but dissolves when the mixture is heated, giving off nitrous gas and forming sulphate of thorina. Sulphide of thorinum is slightly acted on by nitric acid; when dilute sulphuric acid is poured upon it, hydrosulphuric acid gas is given off at first; but the sulphide does not dissolve to any perceptible extent, even when heat is applied.

B. Sulphate of Thorina.—*a. Basic Sulphate.*—An aqueous solution of *b* is mixed with a quantity of ammonia insufficient for complete precipitation. The transparent, gelatinous precipitate is partially converted by washing into hydrate of thorina, and gives up sulphuric acid to the water, the quantity extracted being greater in proportion to the length of time during which the operation is continued, so that, after washing for a short time, the residue contains 23·4 parts, and after long washing, only 17·2 parts of acid to 100 parts of thorina.

*b. Monosulphate.*—Ignited thorina reduced to fine powder is digested for several hours with a mixture of 2 parts of oil of vitriol and 1 part of water, till the latter is evaporated; the excess of sulphuric acid is then expelled by a gentle heat. The residual salt has an earthy appearance.—Mixed with an excess of potassium and heated in a crucible, it is resolved into thorina and sulphide of potassium, the action being attended with violent detonation, and intense ignition of the crucible; the excess of potassium goes off in vapour.

| | Anhydrous. | | Berzelius. |
|---|---|---|---|
| ThO ..... | 67·6 .... | 62·82 .... | 62·77 |
| $SO^3$ ..... | 40·0 .... | 37·18 .... | 37·23 |
| $ThO, SO^3$ | 107·6 .... | 100·00 .... | 100·00 |

The salt dissolves readily in cold water, when a large quantity is added at once; but slowly, when a small quantity only is poured over it, because heat is then evolved. When the solution is evaporated by heat, the bihydrated salt separates; but by spontaneous evaporation at ordinary temperatures, crystals of the pentahydrated salt are deposited.

*α. Bihydrate.*—Formed by evaporating a solution at a temperature above 20° (68° F.), or by heating a cold saturated solution to the boiling point.—Snow-white, woolly mass, consisting of delicate, flexible needles, scarcely soluble in hot water, but dissolving completely, though slowly, in cold water.

*β. Pentahydrate.*—Crystallizes from an aqueous solution by spontaneous evaporation (even when the solution contains an excess of sulphuric acid, which then remains nearly pure in the mother-liquid), in transparent rhombohedrons, which remain unaltered in the air at temperatures under 15° (59° F.); but when kept in dry air, at higher temperatures, part with 3 atoms of water and become milk-white, without however falling to

pieces. In entire crystals, the salt dissolves but slowly in cold water; but when reduced to powder, it dissolves in cold water with greater rapidity and in tolerable abundance. In hot water, the crystals become opaque from formation of $\alpha$, and leave a skeleton in the form of the crystal.—From a cold aqueous solution, the salt $\alpha$ is almost entirely separated on the application of heat; but if other sulphates are present, which form a double salt with it, little or no precipitation takes place. A solution rendered turbid by heat becomes clear again on cooling. From a cold aqueous solution, alcohol throws down the pentahydrate; from a hot solution, the bihydrated salt.

| | | Crystallized. | | | Crystallized. | |
|---|---|---|---|---|---|---|
| ThO | 67·6 | 53·82 | ThO | 67·6 | 44·30 | |
| $SO^3$ | 40·0 | 31·85 | $SO^3$ | 40·0 | 26·21 | |
| 2HO | 18·0 | 14·33 | 5HO | 45·0 | 29·49 | |
| ThO, $SO^3$ + 2Aq. | 125·6 | 100·00 | ThO, $SO^3$ + 5Aq. | 152·6 | 100·00 | |

*c. Acid Sulphate.*—When 100 parts of the salt *b* are heated with oil of vitriol over the flame of a spirit-lamp till no more sulphuric acid passes off in vapour, about 119·77 parts of an acid salt remain (consisting of 1At. of base and about $1\frac{1}{2}$ At. acid).

### Thorinum and Bromine.

*Hydrated Bromide of Thorinum* or *Hydrobromate of Thorina.*—A solution of hydrate of thorina in excess of aqueous hydrobromic acid leaves, when evaporated at ordinary temperatures, a tenacious gum, which, from decomposition of the excess of acid (and formation of hydrobromite) acquires a deep yellow colour.

### Thorinum and Chlorine.

A. Chloride of Thorinum.—A mixture of thorina and sugar is carbonized in a covered crucible, and the carbonaceous mass ignited in a porcelain tube through which a current of dry chlorine gas is passed: decomposition proceeds very slowly. The greater part of the chloride of thorinum is deposited in the form of a white, semifused, crystalline mass, just where the tube ceases to glow; on second sublimation, it yields brilliant colourless crystals. Chloride of thorinum is decomposed by potassium with slight detonation and combustion.

*Hydrated Chloride of Thorinum* or *Hydrochlorate of Thorina.*—Chloride of thorinum dissolves in water with great evolution of heat; it also deliquesces in the air.—Hydrate of thorina dissolves readily in hydrochloric acid; the solution evaporated to a small bulk solidifies on cooling and forms a radiated mass—especially when it contains an excess of acid, which renders the salt less soluble. By evaporation at a gentle heat, a deliquescent saline mass is obtained, which, in a dry atmosphere, neither becomes crystalline nor dries up; but when strongly heated, gives off all its hydrochloric acid and leaves pure thorina. The aqueous solution is not decomposed or rendered turbid by boiling. The salt likewise dissolves in strong hydrochloric acid (differing in this respect from the corresponding zirconium compound), although more sparingly than in water. Both dry and hydrated chloride of thorinum are perfectly soluble in alcohol.

B. Oxychloride of Thorinum.—In the preparation of chloride of thorinum, a white cloud passes over with the chlorine gas, and condenses in the receiver in the form of a white, amorphous sublimate. Water resolves this substance into soluble chloride of thorinum and an insoluble residue of thorina, which does not become visible till the receiver is dried.

### Thorinum and Fluorine.

Fluoride of Thorinum.—When hydrate of thorina is treated with excess of hydrofluoric acid, fluoride of thorinum is deposited in the form of a heavy, white, insoluble powder.—The excess of hydrofluoric acid poured off from the salt contains scarcely anything in solution. Fluoride of thorinum is not decomposed by ignition, and but very imperfectly by potassium.

### Thorinum and Nitrogen.

A. Nitrate of Thorina.—The solution evaporated in a confined space over oil of vitriol dries up to a crystalline mass; when evaporated in the air, it yields a thick syrup. The salt is very soluble in water and in alcohol; the aqueous solution is not rendered cloudy by boiling.

B. Carbonate of Thorina and Ammonia.—The hydrate, carbonate, and basic salts of thorina dissolve sparingly in a dilute solution of carbonate of ammonia; in a concentrated solution, however, they dissolve somewhat copiously. The solution heated to 60° in a close vessel becomes turbid, from separation of thorina, which, however, is slowly re-dissolved on cooling. Caustic ammonia produces no cloudiness in the solution, but on the contrary, restores its transparency when turbid from partial precipitation.

### Thorinum and Potassium.

Thorina cannot be made to unite by fusion with caustic potash or soda, or their carbonates. If the mixture be put into water after ignition, it falls to pieces and forms a white milky liquid; and the finely-divided thorina, like titanic acid, is carried through the filter by the wash-water, unless hydrochloric acid, or sal-ammoniac is previously added to it. Thorina is not rendered soluble in hydrochloric or nitric acid by ignition with alkalis.

A. Carbonate of Thorina and Potash.—The hydrate and carbonate of thorina are slightly soluble in a dilute solution of carbonate of potash, and somewhat copiously in a concentrated solution: the ignited earth is insoluble in that liquid.

B. Sulphate of Thorina and Potash.—1. When crystallized sulphate of potash is immersed in a solution of sulphate of thorina, the liquid gradually becomes turbid, and deposits the double salt in the form of a white, crystalline powder. If the solution is neutral and concentrated, the sulphate of thorina is not completely precipitated, because the sulphate of potash becomes enveloped with a coating of the double salt; but if to the solution of sulphate of thorina, a boiling saturated solution

of sulphate of potash is added, as long as it forms a cloud, the precipitation on cooling is complete, so that the liquid, even though containing an excess of acid, is quite free from thorina: the double salt is however mixed with crystals of sulphate of potash.—2. The salt may also be prepared by fusing together thorina and bisulphate of potash at a red heat. It crystallizes from an aqueous solution by spontaneous evaporation, or from a hot solution, on cooling, in transparent and colourless rectangular prisms, which are permanent in the air at ordinary temperatures, but when gently heated, part with their water of crystallization and become milk-white. The salt dissolves slowly in cold water, but abundantly and with ease in hot water; it is perfectly insoluble in water saturated with sulphate of potash (thereby distinguished from yttria). The aqueous solution, after long continued boiling in a platinum vessel, deposits an insoluble basic salt, while bisulphate of potash remains in the solution; but the decomposition does not go beyond a certain point. The basic salt is very soluble in dilute acids (differing thereby from the corresponding zirconia compound), but not in alcohol. It does not combine by fusion with bisulphate of potash.

| | Crystallized. | | | | Berzelius. |
|---|---|---|---|---|---|
| KO | 47·2 | .... | 23·16 | .... | 23·41 |
| ThO | 67·6 | .... | 33·17 | .... | 33·08 |
| $2SO^3$ | 80·0 | .... | 39·25 | .... | 38·95 |
| HO | 9·0 | .... | 4·42 | .... | 4·56 |
| $KO,SO^3 + ThO,SO^3 + Aq.$ | 203·8 | .... | 100·00 | .... | 100·00 |

C. Bromide of Thorinum and Potassium.—Prepared by mixing bromide of thorinum with bromide of potassium.—White.

D. Chloride of Thorinum and Potassium.—A mixture of the hydrated chlorides of thorinum and potassium is first dried, and afterwards ignited in a current of hydrochloric acid gas. A small portion only of the chloride of thorinum sublimes, or is decomposed by the water still adhering to it.—In combination with water, or as *hydrochlorate of thorina and potash*, it crystallizes irregularly. It is very soluble in water, and almost deliquescent.

E. Fluoride of Thorinum and Potassium.—Precipitated in the form of a white powder on mixing an aqueous solution of a salt of thorina with fluoride of potassium, or with any other salt of potash and free hydrofluoric acid. The salt is not decomposed by ignition; potassium however decomposes it with a slight explosion, but without any emission of light. It is insoluble in water.

F. Nitrate of Thorina and Potash.—The solution evaporated in the air to a syrupy consistence solidifies completely in a fibrous mass. Very soluble in water and in alcohol.

## Thorinum and Sodium.

Thorina does not dissolve before the blowpipe in carbonate of soda. In borax or microcosmic salt it dissolves very slowly; the bead, when saturated with the earth, becomes milk-white on cooling; a less saturated globule remains transparent, and is not rendered turbid, even by flaming.

CHAPTER XIV.

# ZIRCONIUM.

Klaproth. Zirconia. *Beiträge*, 1, 203 and 227.
Guyton-Morveau. Zirconia. *Ann. Chim.* 21, 72.
Vauquelin. Zirconia. *Ann. Chim.* 22, 179.
Berzelius. Zirconia. *Schw.* 21, 40.—Zirconium and Zirconia. *Pogg.* 4, 117.
Pfaff. Zirconia. *Schw.* 28, 102.
Chevreul. Zirconia. *Ann. Chim. Phys.* 13, 245; also *Schw.* 29, 144.
Hermann. *Buchner's Repert.* 35, 117; *Ann. Pharm.* 52, 440, 1844.

*History.* Zirconia was discovered by Klaproth in 1789. In 1824, Berzelius eliminated the metal zirconium from it, and gave a more exact account of its chemical relations.

*Sources.* Rare. Found as an oxide combined with silica in Zircon (and Hyacinth) and in Eudialite; with titanic acid in Polymignite, Aeschinite, and Oerstedite; and with tantalic acid (to the amount of 3 per cent.) in Fergusonite.

*Preparation.* In an iron tube $\frac{1}{4}$ of an inch wide and $1\frac{1}{4}$ inches long, closed at bottom, and contained in a platinum crucible not much larger than itself and furnished with a cover, a mixture of dry powdered fluoride of zirconium and potassium arranged with potassium in alternate layers, is heated over the flame of a spirit-lamp. The heat is applied gently at first—the mixture being frequently stirred with an iron wire; afterwards the temperature is raised to low redness—whereupon, if the double fluoride is perfectly dry, reduction takes place without any noise or appearance of combustion. A tube of glass may also be used instead of an iron tube; but in that case silicium is reduced from the glass, and as the tube cools, cracks off and contaminates the zirconium. The mass when cold is digested in water, on the addition of which, a slight evolution of hydrogen gas takes place, and the zirconium is separated. It is then washed with cold water; and in order to get rid of the hydrate of zirconia mixed with it—which is formed by the action of the potash on the remaining silico-fluoride of zirconium (the potash itself being produced from the potassium by decomposition)—it is, while still wet, digested for six hours at a temperature between 40° and 50°, with a mixture of equal parts of hydrochloric acid and water, which, by slightly acting on the zirconium, gives rise to the evolution of a small quantity of hydrogen gas. The whole is then thrown upon a filter, and

the zirconium washed, first with water containing sal-ammoniac, and lastly with alcohol. (By washing with pure water, the whole of the zirconium would be carried, in a state of minute division, through the pores of the filter. (Berzelius.)—The earlier attempts of Sir H. Davy (*Gilb.* 32, 392) to obtain zirconium were attended with less satisfactory results.

Becquerel (*Ann. Chim. Phys.* 48, 337) introduced into the tube *b* (*App.* 8) a concentrated solution of chloride of zirconium, mixed with a small quantity of chloride of iron (without this, the decomposition would not take place); filled the tube *a* and cup *c* with a solution of common salt; and passed the positive electrode of a voltaic battery of 30 pairs into the tube *a*, and the negative electrode into the tube *b*. The negative platinum wire first became grey, and in the course of 24 hours was covered with steelgrey, four-sided tables, first of zirconium containing iron, but afterwards of pure zirconium. These crystals yielded readily to the blow of a hammer; and were rapidly converted by oxidation into a white mass, not only on exposure to the air, but even in the liquid in which they were produced. This change took place as soon as the current of electricity was interrupted, and was attended with evolution of hydrogen gas. This great oxidability was attributed by Becquerel to the presence of a trace of iron.

*Properties.* Black, coherent powder resembling charcoal in appearance; may be compressed by the burnishing steel into thin, shining scales resembling graphite, of a grey colour and some degree of metallic lustre: these scales, however, do not conduct the current of a hydro-electric pair. Zirconium may be heated in vacuo or in an atmosphere of hydrogen gas to the melting point of glass, without fusing or undergoing any change (but if hydrate of zirconia is present, the metal becomes heated to redness, by absorbing the oxygen of the water combined with the zirconia). Unignited zirconium diffuses itself through water in so fine a state of division, that it passes through the filter; the addition of hydrochloric acid, saline substances, &c., instantly causes it to aggregate into large flakes. But if it be left at rest, and especially if heat be applied, the zirconium separates from the water and falls down to the bottom, but only after a considerable lapse of time. (Berzelius.)

## *Compounds of Zirconium.*

### Zirconium and Oxygen.

### Zirconia. ZrO.

*Zirconerde, Zirkonium-oxyd, Hyacintherde, Zircone.*

*Formation.*—1. Zirconium takes fire in the air at temperatures considerably below redness, and burns with a brilliant light, though tranquilly, and forms zirconia, white and free from potash. If the metal is mixed with hydrate of zirconia, the combustion is attended with a kind of explosion, and the materials are scattered about; if carbon is present, it becomes so surrounded by the earth that it is not consumed, and gives a dusky hue to the zirconia. Zirconium ignited in vacuo, and exposed to the air as soon as it cools, becomes so much heated that it takes fire; but if, after ignition, it is first brought into contact with air in a narrow tube, it neither takes fire at that time, nor when subsequently thrown out into the

air.—2. With the hydrates of the fixed alkalis, hydrate of zirconia, or hydrated borax, zirconium explodes on the application of heat, absorbing the oxygen of the water. Heated with carbonate of potash or soda, it combines with the oxygen of the carbonic acid, the decomposition being attended with a slight explosion. It decomposes chlorate and nitrate of potash, but only at a red heat; a mixture of chlorate of potash and zirconium takes fire when smartly struck, but does not detonate.—3. Aqua-regia, oil of vitriol, and concentrated hydrochloric acid, oxidize zirconium only at a boiling heat and but slowly, the latter evolving hydrogen gas. Hydrofluoric acid dissolves it even in the cold, with disengagement of hydrogen gas; a mixture of hydrofluoric and nitric acids dissolves it with great rapidity. (Berzelius.)

*Preparation.* Zircon (which consists of silica and zirconia, with a very small quantity of sesquioxide of iron) or hyacinth, is, in the first place, very finely pounded: the oxide of iron may then be partially separated by digestion in hydrochloric acid.—As zircon is frequently found mixed with spinelle, garnet, &c., it should be previously ignited—whereby its colour is destroyed, while that of the other gems remains unaltered—and the colourless crystals of zircon picked out. (Berzelius.)—The decomposition and further treatment of the zircon is then conducted as follows:

*a. Decomposition of the Zircon.*—1. Klaproth and Berzelius fuse the pounded mineral at a gentle heat with 4 or 5 parts—Chevreul, and Dubois & Silveira, with 2 parts of hydrate of potash, the materials being put into a silver crucible, and kept at a gentle heat for an hour or two. The cooled mass is then digested in hot water, as long as the water continues to dissolve out any silicate of potash. The insoluble residue consists of silicate of zirconia and potash (*a*, 1) mixed with sesquioxide of iron.—2. Berzelius gently ignites a mixture of one part of zircon and 3 parts of carbonate of potash in a platinum crucible; and introduces hydrate of soda from time to time, in small pieces, into the middle of the mixture—taking care that it does not come in contact with the crucible—whereupon the hydrate fuses and is absorbed by the porous mass. This mode of proceeding prevents the spitting which would otherwise be produced by the escape of the water contained in the hydrate of soda. The covered crucible is then exposed for three quarters of an hour to a heat approaching whiteness.—3. Wöhler (*Berzelius, Lehrb.* 2, 391) introduces an intimate mixture of one part of powdered zircon with 4 parts of dry carbonate of soda into a platinum crucible fitted with a cover; places this in an earthen crucible—the bottom of which is covered with magnesia to prevent the platinum from adhering to it; and ignites strongly for half an hour in a wind-furnace. The mass becomes fused and perfectly disintegrated.—4. Berthier (*Ann. Chim. Phys.* 50, 362; also *Ann. Pharm.* 5, 246) fuses one part of zircon with 3 parts of hydrate of soda at a gentle heat in a silver crucible, or with 3 parts of dry carbonate of soda at a high temperature in a platinum crucible. He prefers soda, because potash produces with the zirconia a double salt which is difficult to decompose. The mass is diffused in a large quantity of cold water; the solution decanted; and the greater part of the soda and silica separated by repeated washing with water, and decantation.—5. Berthier first fuses the zircon at a gentle heat with 2 parts of hydrate of soda in a silver crucible, and then exposes the mass in a charcoal crucible to a full white heat.—6. Berthier also fuses a mixture of 1 part of zircon and 2 parts of carbonate of soda in a silver crucible; reduces the cooled mass to powder; mixes it with 1 part of sul-

phur (to 1 part of zircon), and ignites the mixture in a charcoal crucible at such a temperature that the mass may remain for some time in a pasty state. The reddish-grey, blistered, and somewhat crystalline mass is pounded when cold; then diffused through a large quantity of water freed from atmospheric air by boiling; and the solution, which contains sulphide of sodium together with sulphide of iron, is decanted from the zirconia. The separation of the iron from the zirconia is facilitated by converting the sesquioxide of iron into sulphide.—7. Berthier (*Ann. Chim. Phys.* 59, 192) places a mixture of 10 parts of zircon, 3·3 parts of quartz, and 11·1 parts of marble in a charcoal crucible, and heats it in a blast-furnace. The iron is reduced, and may be detached from the stony mass by the blow of a hammer. One part of zircon likewise fuses completely with 2·4 parts of litharge.—8. Wöhler (*Pogg.* 48, 94) proposes to pass chlorine gas over a mixture of powdered zircon and charcoal ignited in a tube of porcelain or very hard glass, whereby the chloride of silicium will be volatilized and the chloride of zirconium sublimed in combination with zirconia, and in such a state as to be perfectly soluble in hydrochloric acid.

*b. Further treatment of the disintegrated mass.*—1. Klaproth dissolves the powder (*a*, 1) in dilute hydrochloric acid (it requires long digestion and heating); filters to separate any zircon that may remain unacted on; and throws down the hydrate of zirconia—contaminated with hydrated sesquioxide of iron—by means of caustic potash.—2. Chevreul mixes the powder (*a*, 1) with hydrochloric acid to the consistence of a thick paste; introduces it into a long glass tube tapering towards the bottom; and suffers concentrated hydrochloric acid to trickle through it, till that which passes through is no longer blackened by sulphuretted hydrogen—a proof that it no longer contains any silver from the crucible—and till it gives with hydrosulphate of ammonia, a pure white precipitate of hydrate of zirconia, thereby showing the absence of iron. (The hydrochloric acid in passing through dissolves a portion of the zirconia: *Berzelius.*) The chloride of zirconium still remaining in the tube is then dissolved in water; filtered; and the hydrate of zirconia thrown down by ammonia. According to Berzelius, the acid hydrochlorate of zirconia contaminated with iron may be evaporated to the crystallizing point, and the crystals purified from oxide of iron by digestion in concentrated hydrochloric acid, in which they are but very sparingly soluble: the crystals may then be dissolved in water and the solution precipitated as before by ammonia.—3. Dubois & Silveira (*Ann. Chim. Phys.* 14, 111; also *N. Tr.* 5, 2, 439) evaporate the hydrochloric acid solution of (*a*, 1) carefully to dryness; exhaust the residue with water acidulated with hydrochloric acid, which leaves the silica undissolved; and precipitate zirconia and sesquioxide of iron from the filtered solution by excess of ammonia. They then wash the precipitate thoroughly; boil it with solution of oxalic acid; separate the ferric oxalate by filtration and washing, from the insoluble oxalate of zirconia; and either ignite the latter to obtain the pure earth, or decompose it with potash to obtain the hydrate.—4. Berzelius dilutes the hydrochloric acid solution of (*a*, 1) with water, and boils it for a quarter of an hour. Basic hydrochlorate of zirconia free from iron is then thrown down, and may be separated from the acid, either by ignition or by digestion with caustic potash.—5. Or he saturates the neutral solution with sulphate of potash, whereby a basic sulphate of zirconia and potash is formed; washes this double salt with a saturated solution of sulphate of potash; and digests with solution of potash. The zirconia is thereby separated in the form of hydrate, which is washed and dried.—The solution after being treated

with sulphate of potash, still contains a portion of zirconia together with the oxide of iron; both bases may be thrown down by potash; the precipitate dissolved in a small quantity of hydrochloric acid; and the zirconia again separated by the addition of sulphate of potash.—6. Berzelius dissolves the ignited mass (*a*, 2) after cooling, in dilute hydrochloric acid; filters from undecomposed zircon; evaporates the filtrate nearly to dryness; dilutes with water; and separates the solution from the silica by filtration. He then adds an excess of ammonia; dissolves the precipitated hydrates of zirconia and ferric oxide in tartaric acid; supersaturates the liquid with ammonia; mixes the clear solution with bi-hydrosulphate of ammonia, which precipitates the iron in the form of protosulphide; puts the mixture into a stoppered bottle, and leaves it in a warm place till the precipitate has settled down; pours off as much of the solution as possible, and filters the rest—without however washing the sulphide of iron—as a portion of iron might thereby be imparted to the liquid—and finally evaporates to dryness and ignites, till nothing but pure, white zirconia is left behind.—7. Berthier treats the insoluble residue (*a*, 4) with cold, moderately strong hydrochloric acid; adds water, which dissolves nearly the whole; evaporates to a small bulk; separates the solution from the insoluble silica; dilutes it with a considerable quantity of water; and saturates it with hydrosulphuric acid. Any precipitate of sulphide of copper that may be formed (the copper being derived from the silver crucible) must be separated by filtration. The liquid is then mixed with excess of ammonia, which throws down a mixture of hydrate of zirconia and protosulphide of iron; and the precipitate—after being separated from the liquid, by leaving it to subside in a stoppered bottle and decanting—is mixed with such a quantity of aqueous sulphurous acid that the odour of the acid may remain permanent. The sulphurous acid dissolves the whole of the iron in the form of ferrous sulphite. The perfectly white hydrate of zirconia which remains undissolved, is lastly to be washed with water. A small quantity of zirconia is dissolved by the excess of sulphurous acid, together with the oxide of iron; but by boiling the liquid till the excess of acid is expelled, the zirconia is completely precipitated without the slightest admixture of iron.—8. Berthier digests the residue (*a*, 6)—freed by water from the sulphides of iron and sodium—in a small quantity of hydrochloric acid, and thereby dissolves out the rest of the iron and a small quantity of zirconia. The remaining zirconia merely requires to be freed from silica. The small quantity of zirconia contained in the ferruginous hydrochloric acid solution, may be precipitated by the cautious addition of carbonate of ammonia or carbonate of soda, the iron in the liquid being in the state of protoxide.

¶ Scheerer (*Pogg.* 59, 48) fuses zircon with four times its weight of carbonate of soda, and digests the residue in pure water. The water dissolves out silicate of soda, together with the excess of carbonate, and leaves behind a heavy, white, insoluble compound of zirconia and soda, together with light flakes of oxide of iron, oxide of manganese, and other foreign substances, which float about in the liquid when it is agitated. The supernatant liquid is poured off, with as much of the impurities as possible—fresh water added—and the treatment repeated till nothing but the heavy white powder remains. This substance may be collected on a filter and washed, if necessary, but not too long; for it is gradually decomposed by water, zirconia passing through the filter in the peculiar state in which it resists the action of acids. On pouring hydrochloric acid over the salt, it becomes heated, and swells up considerably, but without evolu-

tion of gas. On adding water to the swollen mass, a clear solution is obtained, from which ammonia precipitates pure, snow-white hydrate of zirconia. The precipitate may then be collected on a filter, and thoroughly washed with pure water, to free it from the adhering solution. ¶

The hydrate of zirconia obtained by most of these processes may be converted into the pure earth by ignition.

*Properties.* White powder, rough to the touch; scratches glass (when formed into hard lumps by igniting the hydrate without previously reducing it to powder: *Berthier*). At the heat of a smith's forge, it fuses imperfectly, and forms a grey mass of specific gravity 4·35, which resembles porcelain in appearance, gives sparks with steel, and scratches glass. (Vauquelin.) According to Sir H. Davy, it even scratches rock-crystal. According to Berzelius, pure zirconia is infusible; that which fuses contains potash. In the blowpipe flame, it emits a light of unusual splendour. (Berzelius.) It is tasteless and inodorous.

| | Calculation. | | Berzelius. |
|---|---|---|---|
| Zr | 22·4 | 73·68 | 73·686 |
| O | 8·0 | 26·32 | 26·314 |
| ZrO | 30·4 | 100·00 | 100·000 |

($Zr^2O^3$ = 2 . 420·2 + 3 . 100 = 1140·4. Berzelius.)

*Decompositions.* By the simultaneous action of charcoal and chlorine. By electricity, in the presence of mercury, potassium, or sodium? By potassium at a white heat?

*Combinations.—a.* With water: Hydrate of Zirconia.—For the *preparation*, see that of the earth.—When freshly precipitated, it is a white, bulky, semi-gelatinous mass; when dried, it shrinks up and forms a yellowish, shining, translucent, gummy mass, having a conchoidal fracture. (Vauquelin.)

| | Calculation. | | Berzelius. | H. Davy. | Klaproth. |
|---|---|---|---|---|---|
| 2ZrO | 60·8 | 87·11 | 87·11 | 80 | 66·7 |
| HO | 9·0 | 12·89 | 12·89 | 20 | 33·3 |
| 2ZrO, HO | 69·8 | 100·00 | 100·00 | 100 | 100·0 |

The water is expelled at a temperature considerably below redness; and if the heat be raised to low redness, after all the water has been driven off, the peculiar incandescence first observed by Sir H. Davy is produced (I., 107). According to Chevreul, the incandescence is preceded by blackening. (This, according to Hermann, arises from the presence of impurities.)

*b.* With acids, forming the Salts of Zirconia.—The affinity of acids for zirconia is very slight. Zirconia, which has been heated to incandescence, is no longer soluble in any acid, excepting sulphuric acid: if it be finely pounded, and slowly digested in a heated mixture of 2 parts of oil of vitriol and 1 part of water, till the water and excess of acid are driven off, a residue is left consisting of soluble sulphate of zirconia. The hydrate, when precipitated and washed in the cold, and the carbonate precipitated in the cold, dissolve readily in acids; but, if the hydrate has been precipitated hot, or washed with boiling water, it dissolves only in

concentrated acids, and after long digestion at a high temperature. The hydrate is not soluble in boiling solutions of ammoniacal salts (Berzelius); or in solutions of alkaline carbonates, even when it is freshly precipitated (Hermann). The soluble salts of zirconia have a strong, purely astringent, sour taste, and redden litmus. When strongly heated, they give up their acid, provided the acid is of such a nature that it can be volatilized or decomposed by heat. The precipitates produced in solutions of zirconia-salts by various reagents are as follows: Pure alkalis and alkaline hydrosulphates act upon solutions of zirconia in the same manner as upon the solutions of the preceding earths, thorina perhaps excepted—that is to say—they produce a precipitate of hydrate of zirconia, insoluble in excess of the reagent (and containing a small quantity of the alkali obstinately adhering to it: *Hermann*). The precipitation by the alkaline hydrosulphates is attended with evolution of hydrosulphuric acid. The alkaline carbonates—and carbonate of lime, according to Kobell—give a precipitate of carbonate of zirconia, which is soluble in excess of monocarbonate or bicarbonate of ammonia, potash, or soda, especially if the zirconia-salt be added by degrees to the excess of alkaline carbonate, and the liquid agitated. ¶ Hermann states that, when an alkaline carbonate is added to a neutral solution of zirconia, the first portions give rise to the formation of a soluble basic salt, and a further quantity throws down an insoluble basic salt, with evolution of carbonic acid. This basic salt, however, dissolves in an excess of the reagent, forming a double carbonate. The alkaline sulphites behave in a similar manner. (*Ann. Pharm.* 52, 240.) ¶ Phosphoric acid and phosphate of soda produce a white precipitate of phosphate of zirconia. Sulphate of potash after a short time, even with excess of acid present, throws down basic double sulphate of zirconia and potash, soluble in a large quantity of hydrochloric acid, when precipitated from a cold solution, but scarcely soluble when precipitated from a hot solution. Sulphate of soda causes no precipitation; sulphate of ammonia sometimes only, the precipitate thereby produced being more easily soluble in water and acids. (Berzelius.) Oxalic acid: floculent oxalate of zirconia, soluble in a large excess of hydrochloric acid (Vauquelin, H. Rose); according to Pfaff, oxalate of ammonia precipitates the hydrochlorate, but not the sulphate of zirconia. Alkaline tartrates: white tartrate of zirconia, soluble in caustic potash. Alkaline benzoates and succinates: white benzoate or succinate of zirconia. Tincture of galls: copious white, (Vauquelin), yellow (Berzelius), and—by concentrating the solution—gelatinous precipitate (Chevreul), soluble, according to Vauquelin, in excess of the tincture. The zirconia-salts are not precipitated by zinc or tin (Pfaff); by sulphuric acid, unless potash is also added (Berzelius); by citric acid, or the alkaline citrates, even with the aid of heat (Berzelius); or by ferricyanide of potassium. According to Berzelius, ferrocyanide of potassium likewise causes no precipitate; but according to Pfaff, it produces a greenish-white, and, according to Chevreul, a white precipitate, soluble in excess of the reagent.

## Zirconium and Carbon.

A. Carbide of Zirconium.—Formed when zirconium is prepared with potassium containing carbon. It resembles pure zirconium in external appearance; but, when dissolved in hydrofluoric acid, leaves a residue of carbon; with boiling hydrochloric acid, it evolves hydrogen

gas which smells like that prepared from cast-iron. When burnt, it yields zirconia which is not perfectly white, because a portion of the carbon remains unconsumed. (Berzelius.)

B. Carbonate of Zirconia.—Formed when a salt of zirconia is precipitated in the cold by carbonate of potash. White powder, which according to Klaproth, contains 51·5 per cent. of earth, 7 of acid, and 41·5 of water; according to Vauquelin, 55·5 per cent. of earth, and 44·5 of acid, together with water which is evolved at a gentle heat.

### Zirconium and Boron.

Borate of Zirconia.—Prepared by precipitating a salt of zirconia with borax. White powder, insoluble in water.

### Zirconium and Phosphorus.

Phosphate of Zirconia—White; insoluble in water.

### Zirconium and Sulphur.

Sulphide of Zirconium.—When zirconium is heated in vacuo with sulphur, combination takes place without emission of light and heat; but when the same substances are heated in a vessel full of hydrogen gas, a slight combustion is observed. Dark cinnamon-coloured powder, which does not acquire any lustre under the burnishing-steel, and is a non-conductor of electricity. Fused with potash, it yields zirconia and sulphide of potassium. It dissolves very readily in hydrofluoric acid, giving off sulphuretted hydrogen; in boiling aqua regia it dissolves very slowly.

B. Sulphite of Zirconia.—White, insoluble in water; according to Berthier, however, it is slightly soluble in an aqueous solution of sulphurous acid, from which it is again thrown down on boiling.

C. Sulphate of Zirconia.—*a. Trisulphate.* A solution of the salt *c* is precipitated by alcohol, and the precipitate washed first with alcohol and then with water; or a solution of the salt *b* is largely diluted with water. White flakes, insoluble in water but soluble in hydrochloric acid. (Berzelius.)

| | Calculation. | | Berzelius. |
|---|---|---|---|
| 3ZrO ..... | 91·2 .... | 69·51 ..... | 69·47 |
| $SO^3$ ..... | 40·0 .... | 30·49 ..... | 30·53 |
| $3ZrO,SO^3$ .... | 131·2 .... | 100·00 ..... | 100·00 |

Hermann mentions a sex-basic sulphate.

*b. Disulphate.* Formed by saturating a concentrated solution of the salt *c* with hydrate of zirconia. On evaporating the liquid, a mass of salt is obtained which is gummy and fissured at first, but when further dried becomes white and opaque. The salt, when heated, swells up like alum, and parts with its water; but a white heat is required to expel the acid. The salt dissolves in a very small quantity of water. By a larger addi-

tion of water, the solution is resolved into the salt *a*, which is precipitated, and the salt *c*, which remains in solution. (Berzelius.)

| | Calculation. | | Berzelius. |
|---|---|---|---|
| 2ZrO ..... | 60·8 .... | 60·32 ..... | 60·27 |
| $SO^3$ ..... | 40·0 .... | 39·68 ..... | 39·73 |
| $2ZrO, SO^3$ .... | 100·8 .... | 100·00 ..... | 100·00 |

*c. Monosulphate.*—Zirconia or hydrate of zirconia, free from potash, is dissolved in an excess of sulphuric acid; the solution evaporated to dryness; and the residue heated for a quarter of an hour at a temperature just below redness. The salt loses the whole of its acid at a full red heat.

*Hydrated.*—A neutral solution of the salt yields on evaporation a gummy mass, which, when further dried, becomes white and full of fissures. If, however, the solution contains free acid, hydrated crystals are obtained, which may be freed from adhering acid by means of alcohol. The crystals fuse when heated, giving off their water, and swelling up like alum.

The anhydrous salt dissolves very slowly but completely in cold, and rapidly in hot water. Ammonia added in excess to the solution, precipitates pure zirconia free from sulphuric acid. Alcohol throws down a mixture of the monosulphate and trisulphate, which, after being washed for a considerable time with alcohol, is entirely converted into the trisulphate of zirconia. (Berzelius.) The crystallized salt, as obtained by Vauquelin and Klaproth, contains, according to Berzelius, a small quantity of potash.

| | Calculation. | | Berzelius. |
|---|---|---|---|
| ZrO ..... | 30·4 .... | 43·18 ..... | 43·13 |
| $SO^3$ ..... | 40·0 .... | 56·82 ..... | 56·87 |
| $ZrO, SO^3$ | 70·4 .... | 100·00 ..... | 100·00 |

## Zirconium and Selenium.

Selenite of Zirconia.—White powder, which parts with its acid when ignited. It is insoluble in water, but soluble in an aqueous solution of selenious acid. (Berzelius.)

## Zirconium and Bromine.

*Hydrated Bromide of Zirconium*, or *Hydrobromate of Zirconia.*—A solution of hydrate of zirconia in aqueous hydrobromic acid yields, after evaporation and standing for several days, granular crystals, which have a slightly astringent taste, and are resolved by heat into hydrobromic acid and zirconia. (Berthemot, *Ann. Chim. Phys.* 44, 393.)

## Zirconium and Chlorine.

A. Chloride of Zirconium.—1. Zirconium gently heated in chlorine gas takes fire and burns, forming a white substance which does not volatilize. (Berzelius.)—2. A mixture of zirconia (or zircon) and charcoal, ignited in a current of chlorine gas, yields (besides the chloride of silicium evolved when zircon is used) a white sublimate. (Wöhler

*Pogg.* 48, 94.) Chloride of zirconium prepared by either method, leaves, when digested in water, a portion of zirconia undissolved; in hydrochloric acid, however, it dissolves completely.

*Hydrated Chloride of Zirconium*, or *Monohydrochlorate of Zirconia*.—Chloride of zirconium is dissolved in water, or hydrate of zirconia in aqueous hydrochloric acid, and the solution evaporated to the crystallizing point. The mother-liquor contains the excess of hydrochloric acid, together with a very small quantity of zirconia. Small colourless needles, having a silky lustre and rough taste. In the air at a temperature of 50° (122° F.), they become opaque, and lose half their acid together with their water of crystallization; the other half of the acid is wholly driven off by exposure to a stronger heat. The crystals are readily soluble in water and alcohol, but dissolve very sparingly in concentrated hydrochloric acid. The aqueous solution, however dilute, yields no precipitate on boiling. When it is evaporated to dryness at a temperature of 60° (140° F.), half the acid is expelled, and the salt is converted into an anhydrous residue of di-hydrochlorate of zirconia. (Berzelius.) Hermann likewise mentions the existence of a bi-hydrochlorate and a tri-hydrochlorate of zirconia. (*Vid. seq.*)

B. Hydrated Oxychloride of Zirconium, or Di-hydrochlorate of Zirconia.—A solution of the crystallized hydrochlorate of zirconia gives off part of its hydrochloric acid on evaporation, and leaves a yellowish, gummy mass, containing one atom of zirconia with one atom of chloride of zirconium, besides water. Water dissolves this substance slowly but completely. When the solution diluted with an additional quantity of water is boiled for an hour, it deposits the greater part of the earth as a *still more basic salt*, in the form of a transparent, gelatinous precipitate, which stops up the pores of a filter, and dries up to a yellowish, transparent, fissured mass. (Berzelius.)

## Zirconium and Fluorine.

Hydrated Fluoride of Zirconium, or Hydrofluate of Zirconia.—Hydrofluoric acid continues to dissolve zirconia till the liquid no longer exhibits an acid, but merely a rough taste. By evaporating this solution, a crystalline salt is obtained, which is resolved by water into a soluble *acid* salt and a *basic* salt which remains undissolved. On boiling the solution, a further partial precipitation of the earth takes place, and the liquid becomes still more acid. (Berzelius.)

## Zirconium and Nitrogen.

A. Nitrate of Zirconia.—A solution of hydrate of zirconia in nitric acid, yields on evaporation a yellow, glutinous, gummy mass, which tastes rough and sour, and loses its acid when heated. The salt, after being dried at a temperature not above 100°, is still perfectly soluble in water; and the solution has the power of taking up a large additional quantity of zirconia, in consequence of the formation of a soluble *basic salt*. Hence, a large quantity of alkali may be added to the solution before a permanent precipitate is produced. (Berzelius.) According to Vauquelin, water dissolves only a portion of the residue left by evaporating the nitric acid solution to dryness, the greater part being left

behind in the form of viscid lumps (of basic salt?). Hermann mentions a dinitrate and trinitrate of zirconia.

B. Carbonate of Zirconia and Ammonia.—Monocarbonate or bicarbonate of ammonia dissolves the hydrate of zirconia very slowly and imperfectly, but the carbonate of zirconia with greater facility, especially when small quantities of a salt of zirconia are added to an excess of carbonate of ammonia, and the liquid frequently stirred. But if any of the earth should be precipitated, it often remains undissolved for several hours. On boiling the solution, the zirconia is completely precipitated in the form of hydrate, free from carbonic acid, even before the excess of carbonate of ammonia is driven off. From a solution in bicarbonate of ammonia, the zirconia separates in the form of a white powder; but from the monocarbonate, it is deposited in transparent, gelatinous lumps. (Berzelius, *Pogg.* 4, 143.)

C. Sulphate of Zirconia and Ammonia.—Frequently, but not always precipitated on mixing concentrated solutions of sulphate of ammonia and neutral sulphate of zirconia. Soluble in hot and cold water, and also in acids. (Berzelius.)

D. Ammonio-chloride of Zirconium.—Chloride of zirconium absorbs ammoniacal gas at ordinary temperatures. (Persoz.)

## Zirconium and Potassium.

A. Zirconia with Potash.—Zirconia ignited with hydrate of potash is not thereby rendered soluble in water, which merely separates the excess of potash, but appears to combine with a portion of the alkali, and is rendered soluble in acids. (Berzelius.)

B. Carbonate of Zirconia and Potash.—Hydrate of zirconia is perfectly insoluble in carbonate of potash, and freshly precipitated carbonate of zirconia dissolves but very slowly. When a salt of zirconia is added, drop by drop, to an excess of carbonate of potash, and the liquid frequently agitated, solution takes place immediately; bicarbonate of potash is a better solvent than monocarbonate. Hence, when the former solution is boiled, whereby the carbonic acid is expelled, it deposits a portion of the zirconia in the form of a hydrate. The earth is also deposited, though in small quantity, when the solution is mixed with ammonia, which combines with the excess of acid in the bicarbonate. The rest of the zirconia may be thrown down by boiling the solution with sal-ammoniac. (Berzelius.)

C. Sulphate of Zirconia and Potash.—*a*. Bisulphate of potash in a state of fusion dissolves zirconia, forming a mixture which is perfectly clear while in the fluid state. If a large excess of bisulphate of potash is present, the mass when cold dissolves completely in water; but when the quantity of that salt is smaller, the fused mass is decomposed by water, into bisulphate of potash which dissolves, and the salt *b* which remains undissolved.

*b*. From neutral solutions of zirconia-salts, sulphate of potash, added either in crystals or in saturated solution, gradually separates the whole of the zirconia in the form of a crystalline, basic double salt, while a por-

tion of the sulphate of potash is converted into bisulphate and remains in solution. If excess of acid is present, a portion of the zirconia still remains dissolved, but is precipitated on neutralizing with potash. The same precipitate is likewise produced on mixing sulphate of zirconia with any salt of potash. This salt appears to consist of sexbasic sulphate of zirconia, and likewise contains a very small quantity of sulphate of potash. The zirconia, however, is present in a peculiar state, in which it is less soluble than in its ordinary form. The salt dissolves very sparingly in water, and is again precipitated by sulphate of potash; after being washed with a small quantity of water only, it dissolves with tolerable facility in acids, especially when aided by heat. If, however, it be thoroughly washed, or boiled, either in the liquid from which it is precipitated, or in water, it then becomes nearly insoluble in water and acids, and requires a large quantity of strong acid to dissolve it. After ignition—by which it loses water and sulphuric acid—it is insoluble in boiling oil of vitriol. Fusion with potash renders it only partially soluble in acids; but if it be fused with a large quantity of bisulphate of potash, and then digested in water, the sulphate of potash is dissolved out, and the double salt is left behind in the condition which it exhibits when just precipitated. Solution of ammonia or carbonate of potash decomposes this salt imperfectly; carbonate of ammonia dissolves it, but on boiling deposits it again in its previous state of insolubility in acids. (Berzelius.)

D. Fluoride of Zirconium and Potassium.—*a. With a small proportion of Fluoride of Zirconium.*—Formed when concentrated hydrofluate of zirconia is added drop by drop to an excess of hydrofluate of potash.—*b. With a larger proportion of Fluoride of Zirconium.*—Formed by dropping hydrofluate of potash into an excess of hydrofluate of zirconia.

In both cases, a precipitate is formed, which, when dissolved in hot water, and then evaporated or subsequently cooled, yields small granular crystals, which, at a red heat, neither part with water nor undergo any other change. When heated with potassium, they yield zirconium, and are sparingly soluble in cold, but more abundantly in hot water. (Berzelius.)

Crystallized, *a*.

| | | |
|---|---|---|
| 2K | 78·4 | 32·79 |
| 3Zr | 67·2 | 28·11 |
| 5F | 93·5 | 39·10 |
| 2KF, 3ZrF | 239·1 | 100·00 |

| Or: | Atoms. | | | Berzelius. |
|---|---|---|---|---|
| Potash | 2 | 94·4 | 39·48 | 40·76 |
| Zirconia | 3 | 91·2 | 38·14 | 36·80 |
| Hyp. anhydrous fluoric acid | 5 | 53·5 | 22·38 | 22·44 |
| | 1 | 239·1 | 100·00 | 100·00 |

Crystallized, *b*.

| | | |
|---|---|---|
| K | 39·2 | 27·98 |
| 2Zr | 44·8 | 31·98 |
| 3F | 56·1 | 40·04 |
| KF, 2ZrF | 140·1 | 100·00 |

| Or: | Atoms. | | | Berzelius. |
|---|---|---|---|---|
| Potash | 1 | 47·2 | 33·69 | 32·50 |
| Zirconia | 2 | 60·8 | 43·40 | 43·82 |
| Hyp. anhydrous fluoric acid | 3 | 32·1 | 22·91 | 23·68 |
| | 1 | 140·1 | 100·00 | 100·00 |

### Zirconium and Sodium.

With soda and carbonate of soda, zirconia behaves precisely in the same manner as with potash.

With carbonate of soda, borax, and microcosmic salt, before the blowpipe, it behaves like yttria, except that it dissolves more slowly in the latter salt, and more quickly renders it turbid. (Berzelius.)

### Zirconium and Calcium.

Zirconia with Lime.—Zirconia ignited with lime forms a green, slightly coherent mass. (Morveau.)

### Zirconium and Aluminum.

Zirconia with Alumina.—The two earths may be fused together.

### Other Compounds of Zirconium.

With *iron* and with *mercury*.

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¶ From the experiments of Svanberg, it appears that zirconia is not a simple earth, but a mixture of three, or perhaps even a greater number of metallic oxides; and that these oxides are present in different proportions in the zircons obtained from different localities (*e.g.* Siberia, Norway, and Ceylon), and in the hyacinth from Expailly, in France. The atomic weight of these earths (supposing them to be sesquioxides, expressed by the general formula $R^2O^3$) vary between 75 and 105·6, the mean of which, 91·2, is the atomic weight assigned by Berzelius to zirconia regarded as a simple earth.—No method of completely separating these earths has yet been discovered; but it has been found: (1.) That the oxalate of one of them is less soluble in acids than the oxalates of the rest. (2). That the chloride of the radical of one of the earths is less easily soluble in hydrochloric acid than the corresponding compounds of the other radicals. (3.) That the sulphate of one of them, when mixed with a large quantity of free sulphuric acid, crystallizes much more easily than the sulphates of the rest, and likewise in a peculiar form. To the earth thus distinguished from the others with which it is associated, Svanberg has given the name of *Noria*, from *Nore*, the ancient name of Norway, because the largest quantities of it were obtained from Norwegian zircons. Its radical is called *Norium*. The new earth is likewise found in zircons from the *Ilmengebirg*. (*Pogg.* 65, 317; *Ann. Pharm.* 56, 223.)

Svanberg has likewise discovered that Eudialyte from Greenland contains—besides cerium, lanthanum, and didymium—two other metallic oxides or earths, the first of which closely resembles yttria, and is probably therefore a sesquioxide. The other, which has a yellow colour, is present in very small quantity only. Svanberg is, however, not fully convinced of the separate identity of these earths: indeed, it appears scarcely possible to arrive at any definite conclusion on the subject, until more is known of the nature of yttria and its associated earths. (*Pogg.* 66, 309; *Ann. Pharm.* 56, 225.) ¶

CHAPTER XV.

# SILICIUM.

Scheele: *De Silice, Argilla et Alumine. Opusc.* 2, 67.
Bergman: *De Terra Silicea. Opusc.* 2, 26.
Gay-Lussac & Thénard. Fluoride of Silicium. *Ann. Chim.* 69, 204; also *N. Gehl.* 8, 485; also *Gilb.* 32, 1.
J. Davy. Fluoride of Silicium. *Phil. Trans.* 1812, 352; also *Ann. Chim.* 86, 178.—Further: *N. Edinb. Phil. J.* 17, 243.
Sir H. Davy. Fluoride of Silicium. *Schw.* 2, 57; also *Gilb.* 35, 452. Decomposition of Silica. *Gilb.* 37, 186.
Stromeyer. Reduction of Silicic Acid. *Gilb.* 38, 321.
Berzelius. Silicic Acid and Silicium. *Gilb.* 36, 89;—*Pogg.* 1, 169.
Doveri. *N. Ann. Chim. Phys.* 21, 40.
Kühn. *Ann. Pharm.* 59, 363.
Kopp. *Ann. Pharm.* 67, 356.
Pierre. *Ann. Pharm.* 69, 73.
Scheerer. *Pogg.* 58, 319.
Schaffhäutl. *Ann. Pharm.* 44, 325 and 51, 256.

*History.* At a very early period, minerals of the siliceous class were specially distinguished by the name of vitrefiable minerals. Pott, in 1746, pronounced their chief constituent to be a peculiar earth, whose separate existence and inconvertibility into lime or alumina were established principally by Cartheuser, Scheele, and Bergman. Smithson, in 1811, first regarded this earth as a weak acid. Scheele discovered hydro-fluosilicic acid, and Priestly demonstrated the existence of the gaseous fluoride of silicium. This latter compound was more accurately investigated by Sir H. Davy, J. Davy, Gay-Lussac & Thénard, and especially by Berzelius. In 1823, Berzelius discovered the mode of preparing pure silicium, and a vast number of its compounds previously unknown.

*Sources.* Silicium is, next to oxygen, the most abundant substance on the earth, so far at least as we are acquainted with it; it is found as an oxide, sometimes in the pure state, sometimes combined with other metallic oxides; and in one or other of these states, it enters into the constitution of the greater number of minerals. It occurs in small quantities in the vegetable, and in extremely small quantities in the animal kingdom (as in feathers, &c. *vid.* Besanez, *Ann. Pharm.* 61, 46).

*Preparation.*—1. Potassium is heated in gaseous fluoride of silicium, and the resulting brown substance is washed, first with cold and afterwards with hot water, as long as anything continues to be dissolved. The silicium which remains undissolved, and contains hydrogen and

carbon, is first heated in a covered crucible, at least half filled with it, for a long time and at a temperature just below redness—whereby the hydrogen is expelled and set on fire: afterwards, the cover is removed from the crucible, and the heat raised to bright redness in order to consume the carbon. The silica formed during the ignition is removed by means of dilute hydrofluoric acid, and the residue washed with water and dried. (Berzelius.)—2. Or better: finely divided fluoride of silicium and potassium, or the corresponding salt of sodium—freed from all traces of water by heating it to a temperature considerably above 100°—is arranged in alternate layers with potassium, in a tube of glass or iron closed at one end, and heated over the flame of a spirit-lamp. 10 parts of fluoride of silicium and potassium require from 8 to 9 parts of potassium; if too much potassium is used, silicide of potassium is produced, which dissolves completely in water. As soon as the potassium is fused, it is mixed up with the fluorine compound by stirring with an iron wire, after which the heat is increased. Reduction takes place before the mass becomes red-hot, with a hissing noise and slight appearance of flame. The brown mass, when cool, is repeatedly exhausted with large quantities of cold water, till the liquid no longer exhibits an alkaline reaction. The silicide of potassium produced, gives up potash to the water, and liberates hydrogen gas, while silicium containing hydrogen is deposited; if only small quantities of water are used, a concentrated solution of potash is formed, which oxidizes and dissolves the silicium. —The mass is boiled with water to separate the undecomposed fluoride of silicium and potassium; and the silicium is washed with boiling water, till a few drops evaporated on platinum foil no longer leave any trace of residue (the washing occupies several days, and requires a large quantity of water), and the silicium, after being dried, is freed as in the first method, from hydrogen and silica. (Berzelius.)—3. A bulb blown in the middle of a glass tube is partially filled with potassium, and on this a quantity of chloride of silicium is dropped. To one end of the tube, a retort containing chloride of silicium is then attached, and heated till the liquid boils; at the same time, the potassium is exposed to the flame of a small spirit-lamp, in order that the evaporation of the chloride of silicium which adheres to the potassium, may expel the air from the tube. As soon as the potassium is dry, it takes fire in the chloride of silicium vapour, which is allowed to pass over it freely. Towards the close of the operation, the bulb is heated to redness. As soon as the apparatus is cold, the whole of the chloride of silicium vapour is expelled from the tube by a current of dry air, and the chloride of potassium dissolved out from the mass with water, leaving the silicium behind. (Berzelius, *Lehrb.* 1, 327.)

The earlier experiments of Sir H. Davy do not appear to have yielded pure silicium. Still less satisfactory are those of Clarke and Mantell. (*Gilb.* 62, 391; and *Ann. Phil.* 11, 310 & 393.) It is true that silica is decomposed by ignition with potassium; but the silicium thus obtained is combined with potassium; and in that state, the greater part of it dissolves on the addition of water. (Berzelius.)

*Properties.* Dark-brown powder (lighter before ignition), destitute of lustre, even after being rubbed with the burnishing-steel; leaves a powerful stain; adheres tenaciously to the surface of glass. Heavier than oil of vitriol. Infusible before the blowpipe. Does not conduct the electricity of a hydro-electric circuit. (Berzelius.) This property cannot,

however, be regarded as positively at variance with the supposed metallic nature of silicium: for this element has hitherto been obtained only in a state of minute division. Aluminum and zirconium are likewise non-conductors; and so, likewise, according to Wöhler, is finely divided iron, as it is obtained by igniting the oxalate of the protoxide, or by mechanical subdivision. Neither can the absence of metallic lustre (which is likewise not possessed by zirconium) decide the question whether silicium is a metal or not, as long as it is known only in the pulverulent state. With regard to the chemical relations of silicium, its resemblance to boron must be taken into account on the one hand, and its resemblance to the earth-metals and titanium on the other.

¶ Berzelius distinguishes two allotropic conditions of silicium, which he regards as the cause of the different modifications observed in its compounds. The first, *Si* α, is formed when silica is reduced by potassium: it burns with a vivid flame when slightly heated in the air; detonates when thrown on fused nitre; evolves heat and volatilizes when treated with hydrofluoric acid; unites with sulphur when gently heated with it, the resulting compound being decomposed by water, with disengagement of hydrosulphuric acid, and formation of silica which is soluble in water, and to a greater extent in hydrochloric acid. The second modification, *Si* β, is produced by exposing *Si* α to a strong red heat in a close vessel: it may be heated to whiteness before the blowpipe without taking fire: hydrofluoric acid has no action on it, and it cannot be made to combine with sulphur. Hence, Berzelius concludes that the radical of quartz, rock-crystal, and the insoluble forms of silica artificially prepared, is *Si* β, the peculiar properties of which are still visible in its compounds; whereas the radical of the sulphide and other compounds of silicium which yield the soluble modification of silica, is *Si* α. The existence of two or more allotropic states of an element, with corresponding modifications in the properties of the compounds, is likewise observed in several other elementary bodies, viz., phosphorus, arsenic, tellurium, chromium, titanium, uranium, and manganese. (*Ann. Pharm.* 49, 247.) ¶

## *Compounds of Silicium.*

### Silicium and Oxygen.

### Silica, Silicic Acid. $SiO^2$*.

*Oxide of Silicium, Vitreous Earth, Kieselerde, Silice.*—Found perfectly, or nearly pure, in Beryl, Quartz, Flint, Chalcedony, Hornstone, Jaspar, Opal, &c.

* If silica be regarded as SiO, the atomic weight of silicium will be = 7·5, and that of silica = 15·5; if the formula of Berzelius, $SiO^3$, be adopted, the combining number of the metal will be 22·5, and that of the earth 46·5. The theory which regards silica as $SiO^2$, has been adopted by Gaudin (*Ann. Chim. Phys.* 52, 125), and more especially by Kühn (*Stöchiometrie*, III). It is recommended—as the following pages will prove—by the much greater simplicity of the formulæ, which it yields for the compounds of silicium, both natural and artificial. For the calculations of the latter, the careful collection of mineral analyses in Rammelsberg's *Wörterbuch des chemischen Theils der Mineralogie* (*Dictionary of the Chemical part of Mineralogy*) has been of great service.

¶—Paul Einbrodt, in a paper on the atomic weight of silicium (*Ann. Pharm.* 55, 332), concludes that the formula for silicic acid or silica, is $SiO^2$: First, from

*Formation.* Silicium which has been freed from hydrogen, and rendered coherent by gradual exposure to a white heat, does not take fire at a red heat, either in the air or in oxygen gas; previously to this, it is inflammable. It explodes with hydrate of potash or soda when heated to the melting-point of the alkali, the combination being attended with vivid incandescence, and evolution of hydrogen gas which immediately takes fire; it likewise exhibits ignition with hydrate of baryta; with hydrate of lime the ignition is but faint. It oxidizes with vivid incandescence, when heated with carbonate of potash or soda, the mass swelling up, giving off carbonic oxide gas, and turning black from separation of carbon. The larger the excess of silicium, the more easily is the decomposition effected (even below redness); the more vivid, also, is the incandescence, and the greater the amount of carbon separated. If the alkaline carbonate predominates, no flame is visible, and no carbon is set free, carbonic oxide alone being evolved.

the density of the vapour of the chloride and fluoride of silicium; and 2ndly, from the behaviour of quartz with alkaline carbonates.

1. The calculated densities of chloride and fluoride of silicium, according to the two formulæ, and the densities of the same compounds, as found by Dumas, are as follows :—

| | | | |
|---|---|---|---|
| $SiCl^3$ | 4·44 | $SiF^3$ | 2·710 |
| $SiCl^2$ | 5·933 | $SiF^2$ | 3·617 |
| *By experiment* | 5·939 | *By experiment* | 3·60 |

Moreover, instead of 7 volumes being condensed into 3 volumes, the second calculation requires 5 volumes to be condensed into 2; or 3 volumes into 2, if the combining volume of chlorine be taken as 1, the hypothetical combining volume of silica being $\frac{1}{2}$.

2. When finely divided quartz is fused with excess of carbonate of potash, the evolution of carbonic acid ceases as soon as a silicate is formed, in which the proportion of oxygen in the base is to that of the acid as 1 : 2. Hence, according to the formula $SiO^2$, one atom of silica expels one atom of carbonic acid; whereas, according to the formula $SiO^3$, the silica must expel $1\frac{1}{2}$ atoms of carbonic acid; or 2 atoms of a neutral silicate form a basic salt, and expel an additional atom of carbonic acid at the expense of an additional atom of the alkaline carbonate, which is decomposed, and the carbonic acid expelled.

Kopp, on the contrary, prefers the formula $SiO^3$ for silica, and the corresponding formulæ $SiCl^3$ and $SiBr^3$ for the chloride and bromide of silicium, on the ground that the two latter compounds exhibit just such a difference in their boiling points, as should result from the substitution of 3 atoms of bromine for 3 atoms of chlorine. For, by comparing various compounds of bromine and chlorine, it is found that for every atom of bromine substituted for chlorine, the boiling point rises 32° C., so that the boiling point of bromoform, $C^2HBr^3$, being, according to Cahours, 152°, that of chloroform should be 56°, or 96° lower. Now, the boiling point of chloroform in contact with water, observed by Liebig, is 57°. Again, $PCl^3$ boils, according to Dumas, Pierre, and Andrews, at 78°; $PBr^3$, according to Pierre, at 175°—the calculated temperature being 174° (= 78° + 96°). Now, Pierre finds that the boiling point of chloride of silicium is 59°, and that of the bromide 150°,—a difference of 94°. Hence it may be inferred that in bromide of silicium, 3 atoms of chlorine are replaced by 3 atoms of chlorine, and, therefore, that the formulæ of these compounds are $SiBr^3$ and $SiCl^3$, and the corresponding formula of silicic acid, $SiO^3$. The boiling points of chloride and bromide of silicium as observed by Serullas—though less accurate than those obtained by Pierre—likewise confirm the above view, the degrees being respectively 50° and 148°...150°, a difference of 98°...100°. (Kopp, *Ann. Pharm.* 67, 356.)

Pierre (*Ann. Pharm.* 69, 73) has shown that by the action of hydrosulphuric acid on chloride of silicium at a high temperature, the compounds $SiSCl^2$, $SiS^2Cl$, and $SiS^3$ may be formed; and as the formation of these substitution products is easily explained on the supposition that chloride of silicium is $SiCl^3$, whereas the explanation becomes very complicated if the formula SiO or $SiO^2$ is adopted, he concludes that the chloride is really $SiCl^3$, and consequently that silicic acid is $SiO^3$. If this be admitted, the atomic weight of silicium deduced from Pierre's experiments is 21·34. ¶

With nitre, silicium is oxidized only at a strong red heat, and then indeed with violence. If silicium is fused with nitre, and carbonate of soda added, an explosion follows, and a black mass is formed, which gradually becomes white in the fire. Chlorate of potash thrown on ignited silicium does not oxidize it. A mixture of aqueous hydrofluoric and nitric acids dissolves silicium rapidly, with violent evolution of nitric oxide. Borax in a state of fusion, water, sulphuric acid, hydrochloric acid, hydrofluoric acid, nitric acid, aqua-regia, and aqueous solution of potash, do not oxidize silicium after it has been ignited. Before ignition, on the contrary, it is dissolved by a concentrated solution of potash and by aqueous hydrofluoric acid. (Berzelius.)

*Preparation.* 1. A siliceous mineral, as quartz or flint, is reduced to powder, and fused with three times its weight of carbonate of potash; the fused mass treated with dilute hydrochloric acid; the solution evaporated to dryness; the residue boiled with water containing hydrochloric acid; then washed with pure water; and the insoluble residue ignited. Fuchs precipitates the silica from the alkaline solution by adding sal-ammoniac, and washes it thoroughly with hydrochloric acid, and then with water. —2. Gaseous fluoride of silicium is passed into water, and the precipitated silica thoroughly purified and ignited.

*Properties. a. Crystallized Silica.*—To this variety belong rock-crystal, quartz, amethyst, cacholong, iron-flint, jasper, siliceous slate, hornstone (the latter of which also contain sesquioxide of iron, alumina, lime, magnesia, and soda, probably in the form of siliceous salts). Chalcedony and flint consist, according to Fuchs (*Pogg.* 31, 577), of a mixture of crystallized and amorphous silica; when treated with solution of potash, which dissolves out the amorphous silica, they become opaque and similar to cacholong. Crystallized silica belongs to the rhombohedral system of crystallization; the primary form being an obtuse rhomb. *Fig.* 141; also *Fig.* 131, 137, 138, and other forms. $r^1 : r^3$ or $r^3$ (*Fig.* 141) $= 85° 36'$; $r^3 : r^3 = 94° 24'$; $r^1 : r^2$ or $r^2 : r^3$ (*Fig.* 131) $= 133° 48'$; $r : o$ (*Fig.* 137) $= 141° 40'$; and so on. Cleavage indistinct, parallel to the $r$-surfaces (*Fig.* 141). (Hauy.) Very hard, but softer than diamond, sapphire, or topaz. Specific gravity of rock-crystal = 2·652 at 4°, in vacuo. (Le Royer & Dumas.)

[On the pretended formation of quartz crystals in Carrara marble from a gelatinous solution, see Ripetti (*Schw.* 53, 199).] Bergmann observed cubical crystals (rhombohedrons?) deposited from an aqueous solution of hydrofluate of silica containing excess of acid after the lapse of two years; but they were less hard than quartz. Siegling obtained from a solution of silica exposed to the air for eight years, four-sided pyramids which emitted sparks with steel, and were not attacked by acids. Whether these crystals were really pure silica, has not been determined. When iron smelting-furnaces are opened, there is often found at the bottom a white substance, which Vauquelin has found to consist of silica, probably formed by the combustion of reduced silicium. It is commonly of a very fine fibrous texture (partly concentric, partly arranged in tufts), loose, friable, and of a silky lustre; sometimes of a spherical conformation; rarely earthy. (*Vid.* Grignon, *Mémoires de Physique;* Vauquelin, *Ann. Chim.* 73, 102; and *Ann. Chim. Phys.* 31, 332; Koch, *über Krystallinische Hüttenproducte*, Götting. 1822.) A similar fibrous variety of silica has been discovered by Herr Karl Stumm, accompanied by metallic titanium,

in the iron-furnaces of Fischbach at Saarbridge, and presented by him to the author; it dissolved readily in a hot solution of potash, leaving only a slight turbidity.

¶ Doveri (*Ann. Chim. Phys.* 3, 21, 40) prepares crystallized silica by precipitating chloride of copper with silicate of potash; then filtering, washing the precipitate with water, and dissolving it in hydrochloric acid. From the solution he throws down the copper by means of hydrosulphuric acid, and evaporates the filtered solution of silica in hydrochloric acid, in vacuo over caustic lime. By this means, hydrated crystals of silica are obtained in the form of white, transparent needles, of great lustre, mixed, however, with amorphous hydrate of silica. The needles retain their form, even when perfectly dehydrated. ¶

*b. Amorphous Silica.*—Found native in the form of *Opal*, frequently accompanied by small quantities of potash, soda, lime, magnesia, alumina, and sesquioxide of iron, together with between 5 and 10 per cent. of water. *Hyalite* is pure silica, with 6·33 per cent. of water. Opal was formerly regarded as a hydrate of silica; but the water appears to be only mechanically combined with it; for its quantity is too small for the formula $SiO^2, HO$, or even for $2SiO^2, HO$, and varies greatly in different kinds of opal; moreover, ignited opal presents the same appearance, and has nearly the same degree of solubility in caustic potash as that which has not been ignited. Many varieties of opal likewise contain crystallized silica mechanically mixed; and when the amorphous silica is dissolved, the crystallized portion remains as a skeleton in the original form of the opal. (Fuchs.) Opal is semi-transparent or pellucid; refracts light singly; has a specific gravity of only 2·09, on account of its porosity; and is much softer than quartz. Artificially prepared silica is also amorphous after ignition. (Fuchs.) It is a white, tasteless powder, rough between the fingers, and does not adhere to the tongue; according to Kirwan, its specific gravity is 2·66. Amorphous silica is chemically distinguished from the crystalline variety by its property of combining more readily with the fixed alkalis in the wet way. (Fuchs.) [Vid. *Silicate of Potash, Soda, and Lime.*]

Silica, whether natural or artificial, crystallized or amorphous, fuses in the flame of a spirit-lamp fed with oxygen gas, or in the oxy-hydrogen blowpipe flame, and forms a clear bead. (Marcet, Stromeyer, Clarke.) Sir H. Davy fused it in the circuit of a powerful voltaic pile. Silica in a state of fusion may be drawn out in long threads like glass. Fused rock crystal dropped into water, solidifies to a transparent mass, free from flaws, and remarkably hard and tough, so that it sustains the blow of a hammer without breaking; showing that it has become hardened, just as steel is hardened by sudden cooling. (Gaudin, *J. Pharm.* 25, 392; also *Ann. Pharm.* 31, 351.) Jeffreys (*N. Bibl. Univ.* 29, 417; also *Ann. Pharm.* 39, 255) passed steam into a large furnace containing earthenware heated to a temperature above the melting point of cast iron. By this means, more than 200 pounds of the silica was volatilized with the steam, some pounds of it being deposited in the form of snow, at the spot where the steam entered. This behaviour of silica (if confirmed) is similar to that of boracic acid, which, though not volatile by itself, volatilizes with the vapour of water, alcohol, &c. Silica in all its forms is tasteless, inodorous, and destitute of action on vegetable colours.

Before the blowpipe, silica expels the carbonic acid from carbonate of soda, with effervescence, yielding a transparent glass; in microcosmic salt it is almost wholly insoluble.

Calculation.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Si | 7·5 | Si | 15 | Si | 22·5 | .... | 46·39 |
| O | 8·0 | 2O | 16 | 3O | 24·0 | .... | 51·61 |
| SiO | 15·5 | $SiO^2$ | 31 | $SiO^3$ | 46·5 | .... | 100·00 |

| | Berzelius (mean). | | H. Rose. | | Stromeyer. |
|---|---|---|---|---|---|
| Si | 48·275 | .... | 49·72 | .... | 46 |
| O | 51·725 | .... | 50·28 | .... | 54 |
| | 100·000 | .... | 100·00 | .... | 100 |

*Decomposition.*—By potassium at a white heat, into silicate of potash and silicide of potassium; by carbon, in presence of iron, copper, or silver, at a white heat, into carbonic oxide and silicide of iron, copper, or silver; by hydrofluoric acid, into fluoride of silicium and water; not, however, by any other hydrogen acid, nor by sulphide of carbon at a red heat.

*Combinations.*—*α.* With Water.

*α.* Hydrate of Silica.—Formed when an aqueous solution of silicate of potash is precipitated by an acid, by sal-ammoniac, or by a metallic salt, such as sulphate of copper (in the latter case, a mixture of hydrate of silica and a metallic silicate is formed; and on removing the latter by means of dilute hydrochloric acid, the hydrate of silica remains undissolved: *Doveri*); or when the silica held in solution by an aqueous acid, is precipitated by a soluble alkali or alkaline carbonate; or when a solution of silica in hydrochloric or nitric acid is partially evaporated; or when fluoride of silicium is decomposed by water. After washing the gelatinous precipitate with hydrochloric acid and then with water, the hydrate is obtained in a state of purity. When newly formed, and as long as it continues saturated with the aqueous solution, it presents the appearance of a tenacious, pellucid jelly (*Kiesel-gallerte*), or of gelatinous flakes; but when dried in the air, even at ordinary temperatures, it not only loses the water which adheres to it, but also that which is chemically combined with it, and is converted into a white powder, consisting of anhydrous silica. ¶ Doveri states, that when dried in the air at ordinary temperatures, it retains between 16·9 and 17·6 per cent. of water, corresponding to the formula $SiO^2$, HO; but when dried at 100°, it loses water, and the remaining hydrate has the formula $2SiO^2$, HO. ¶

*β. Solution of Silica.*—Many springs contain silica in solution. Anhydrous silica is wholly insoluble in water. According to Kirwan, hydrate of silica dissolves in 1000 parts of water, and with peculiar facility when in the nascent state. The gelatinous silica obtained in the decomposition of fluoride of silicium by water, dissolves in a considerable quantity of water, forming a tasteless solution which does not redden litmus; and, on evaporation, deposits the silica in the form of a white, non-crystalline powder. Silica thus prepared is in a peculiar state, for it dissolves again in water. If sulphuric or hydrochloric acid is added to the solution before evaporation, the silica which remains is insoluble. (Berzelius, *Lehrb.* 2, 122.) By allowing crystallized boracic acid to absorb gaseous fluoride of silicium, and then separating the hydrofluoric and boracic acids by digestion with a large excess of ammonia, a hydrate of silica remains, which, after being thoroughly purified from the above acids, is very soluble in water. The aqueous solution does not act on

vegetable colours, and gives no precipitate when boiled; on evaporating to dryness, however, the silica remains as an insoluble powder. (Berzelius, *Ann. Chim. Phys.* 14, 366.)

*b.* With Acids, yielding the SALTS OF SILICA. Of all the oxides of the light metals, silica exhibits the feeblest basic properties; in the anhydrous state, it is insoluble in all hydrated acids, excepting hydrofluoric acid. Sulphuric, nitric, and hydrochloric acid, for example, do not dissolve it; the same acids dissolve the gelatinous variety, but very slowly and in small quantity only. They dissolve the largest quantity when a compound of silica with a fixed alkali, in which the latter predominates, is mixed with an excess of the acid in a state of great dilution—so that the earth, at the moment of its separation from the alkali, meets with a sufficient quantity of acid and water to dissolve it. The clear liquid, however, always contains several atoms of acid to one of the earth, and the acid is never neutralized. From the solution, ammonia and its carbonate, and likewise potash or soda, precipitates a portion of the silica in the gelatinous state. Carbonate of lime precipitates the silica, chiefly when the solution is warm and not too dilute; the gelatinous lumps which separate are insoluble in acids. If, however, the solution likewise contains another base which is precipitable by carbonate of lime, such as alumina or sesquioxide of iron, the carbonate of lime throws down a compound of the base with the silica, which compound is again perfectly dissolved by hydrochloric acid, and yields a gelatinous precipitate on evaporation. (Von Kobell, *Schw.* 60, 297.) When a solution of silica in any volatile acid (excepting hydrofluoric acid) is evaporated, the acid and water go off together, leaving hydrate of silica in the form of a jelly at first; but after evaporation to dryness, the residue consists of pure silica, which, when perfectly dry, is insoluble both in water and in acids.

*c.* With strong Salifiable Bases, forming salts called SILICATES, inasmuch as the silica in these compounds plays the part of a weak acid. Silica decomposes the alkaline carbonates at a low red heat; and at very high temperatures, even the sulphates are decomposed by it. A vast number of silicates are found in nature, constituting in fact the greater part of the mineral kingdom. Many of these compounds may be obtained artificially, by fusing together their component parts, and in the same crystalline form as that which they exhibit in their native state. (Mitscherlich; Berthier, *Ann. Chim. Phys.* 24, 355.) Many other silicates are exclusively artificial products, and are, for the most part, obtained by fusing their ingredients together. The simple salts of silicic acid generally solidify in the crystalline form on cooling; silicate of lead, however, is an exception. The double salts, on the contrary, become viscid when fused, and yield a glass. Silicic acid combines with bases in an unusually great variety of proportions; the most common are the following: 1 At. base to $\frac{1}{2}$, 1, 2, 3, and 4 At. acid. It forms numerous double salts, the most abundant of which are compounds of silicate of alumina with another salt of silicic acid (felspar). There are also a great number of hydrated silicates, both simple and compound. The different kinds of zeolite consist of hydrated combinations of silicate of alumina, with another silicate of the potash or magnesia class.

The silicates are more easily decomposed by acids, as the hydrochloric—the stronger the base—the less the silica predominates in the compound

—and the larger the proportion of water present; hence many minerals containing water—zeolite for example—lose their solubility in hydrochloric acid after ignition. The hydrochloric acid either dissolves the base, and separates the silica in a pulverulent or gelatinous form, according to the nature of the compound; or it likewise dissolves the silica either wholly or in part, especially when a large quantity of water is present, and in that case yields a jelly on evaporation. Sulphuric acid diluted with a small quantity of water, decomposes, after long digestion, nearly all the salts of silicic acid, when reduced to powder. All silicates without exception become soluble in dilute hydrochloric or nitric acid, after fusion with from 3 to 5 times their weight of hydrate of potash or soda, carbonate of potash or soda, or of baryta, strontia, lime, or oxide of lead. They are completely disintegrated; and the solution yields, on evaporation, first a jelly and then a dry residue, of which the part which is insoluble in hot hydrochloric acid, exhibits the characters of silica. Andalusite, Cyanite, Staurolite, and Zircon, require a full white heat, to disintegrate them perfectly with an alkaline carbonate, and are more readily acted on by hydrate of potash. From the native silicates, whether simple or double, which contain potash, soda, or lithia, lime separates the more soluble alkali, by the so-called *fluid cementation*. (Fuchs.) The silicates are sometimes ignited, after being mixed with lime, and then treated with water; but in many cases, as with Nepheline, Leucite, Natrolite, Analcime, and Chabasite, it is sufficient to ignite them by themselves, and afterwards boil them in a finely divided state with milk of lime, or to digest them with it for a longer time in the cold. Clays treated in this manner likewise give up to water the small proportion of potash or soda which they contain; and if they happen to be rich in carbonate of lime, they merely require to be digested in water after ignition. Volcanic rocks, such as phonolitic lava, give up their potash or soda, by digestion with milk of lime, even without previous ignition. (Zierl. *J. Techn. Chem.* 10, 280.)

Pulverized silicates heated in a platinum vessel with fluor-spar free from silica and oil of vitriol, evolve gaseous fluoride of silicium, which, when the vessel is covered with moistened felt, deposits upon it white flakes of hydrate of silica.—The same gas is evolved, with heat and effervescence, when a powdered silicate is immersed in a strong solution of hydrofluoric acid. The residue evaporated to dryness with sulphuric acid leaves the base of the silicate in combination with the sulphuric acid.—Microcosmic salt in the blowpipe-flame withdraws the base from the silicates, and sets the silicic acid free. The product is a translucent, blistered mass. (*Kieselskelett.*) — When a small quantity only of the microcosmic salt is used, the fused mass diffuses itself through the siliceous crust; when the quantity of flux is larger, the silica floats in the fused bead. When only a small quantity of silica is present, the glass is clear while fused, but becomes turbid on cooling; with still less silica, however, it remains transparent. (Berzelius.)—Silicates heated with carbonate of soda before the blowpipe, expel the carbonic acid with effervescence. The silicates of the more soluble alkalis and of most of the oxides of the heavy metals, yield a transparent glass; those of the earthy alkalis and of the earths, yield, sometimes a clear and sometimes a turbid glass, according to the proportions of silica and of acid. If the silicic acid contains at least twice as much oxygen as the earth, the *latter* is dissolved in the glass by the agency of the silicic acid, and the *glass remains* clear. If the compound contains less silica, it yields a clear

glass with a comparatively small proportion of carbonate of soda; but with a larger proportion, it forms a turbid glass; and with a still larger quantity, an infusible slag: for, the greater the amount of soda, the greater also is the quantity of the earthy base which is separated by its action from the silicic acid. (Berzelius.)—All the salts of silicic acid are insoluble in water, excepting the silicates of potash, soda (and lithia ?).

### Silicium and Hydrogen.

Hydride of Silicium.—Fluoride of silicium is decomposed by potassium, and the brown mass washed with water; a portion of the hydrogen set free in the decomposition of water by the excess of potassium combines with the silicium, forming hydride of silicium; and by treating this mass with a cold aqueous solution of hydrofluoric acid, the compound is obtained free from silica. This substance burns with great splendour when quickly heated to redness in the air. In oxygen gas, the combustion is still more brilliant. Only a third part of the silicium burns in the air, and three-fourths in oxygen gas, because the rest becomes surrounded with the silica which is produced. During the combustion, water is invariably formed, even after the silicium has been dried in vacuo at a temperature approaching redness. Hydride of silicium heated in a covered crucible, emits a feeble flame when the cover is taken off. A hot solution of hydrofluoric acid or of potash dissolves a small quantity of silica, with evolution of hydrogen gas. When the compound is very slowly heated to incipient redness in an open crucible, and then to whiteness in a covered crucible, the hydrogen is expelled, and a residue of pure silicium is left, mixed only with a small quantity of silica, formed during the operation. (Berzelius.)

### Silicium and Carbon.

*Carbide of Silicium ?*—If silicium is reduced from the double fluoride of silicium and potassium, by potassium prepared according to Wöhler's method (III., 5), and freed from carbon by re-fusion only and not by distillation, a mixture of silicium and carbide of silicium is obtained, of a darker colour than pure silicium. This substance, when ignited, suffers no loss of weight, but yields carbonic acid gas, and a mixture of silica and unburned silicium free from carbon. (Berzelius.)

### Silicium and Boron.

Boracic acid in a state of fusion dissolves little or no silica.

### Silicium and Phosphorus.

Silicium does not combine with phosphorus when ignited in its vapour. (Berzelius.)

### Silicium and Sulphur.

A. Sulphide of Silicium.—Formed by igniting silicium in vapour of sulphur, or by passing vapour of sulphur over silicium at a white heat: the combination is attended with incandescence.—Sulphide of silicium is white and earthy, or—if silicium be present in an uncombined state—

dark grey and drossy. It burns slowly when heated in the air, forming sulphurous acid and silica; in a cold dry atmosphere, it remains unchanged; in ordinary moist air, it emits a powerful odour of sulphuretted hydrogen, and is gradually converted into silica. Water instantly decomposes it into hydrosulphuric acid which escapes as gas, and silica which is dissolved; with a small quantity of water, so concentrated a solution of silica is obtained, that the whole gelatinizes, after slight concentration, and on drying yields a transparent fissured mass of silica.—Sulphide of silicium is capable of uniting with sulphide of potassium. (Berzelius.)

B. Sulphate of Silica.—Obtained in solution, by supersaturating silicate of potash with very dilute sulphuric acid.

### Silicium and Iodine.

Silicium ignited in iodine vapour does not absorb any of the iodine. (Berzelius.)

### Silicium and Bromine.

Bromide of Silicium.—A pasty mixture of silica, lamp-black, sugar, and oil—in such proportions that the carbon produced may amount to at least one half the quantity of the silica—is ignited in a covered crucible; the resulting mass introduced in small pieces into a porcelain tube having one of its ends connected with a retort containing bromine, and the other with a projecting tube passing into a tubulated receiver surrounded with ice; and vapour of bromine made to pass gradually through the ignited porcelain tube. The carbonic oxide gas escapes through a long, fine-drawn tube inserted into the tubular opening of the receiver; and the bromide of silicium mixed with excess of bromine collects in the receiver itself. The whole is then poured into a retort with mercury, and the bromide of silicium separated by distillation from the bromide of mercury. Colourless liquid, much heavier than oil of vitriol; freezing at — 12° ... — 15° (+ 10·4° ... + 5° F.), and boiling at 148° ... 150° (298·4° ... 302° F.). Forms dense white fumes in the air, and has an acrid, disagreeable smell. It has likewise an ethereal odour, which Serullas attributes to the presence of bromide of carbon. Water rapidly decomposes bromide of silicium, with considerable elevation of temperature. Under oil of vitriol, it is resolved, in the course of a few days, into silica and bromine. When gently heated with potassium, it explodes violently and breaks the glass tube. (Serullas, *J. Chim. Med.* 8, 1; also *Ann. Chim. Phys.* 8, 1; also *Pogg.* 24, 341.)

### Silicium and Chlorine.

A. Chloride of Silicium.—1. When ignited silicium, or silicium containing hydrogen, is heated in chlorine gas, it takes fire and continues to burn till the whole has disappeared. The product is chloride of silicium in the form of vapour, which solidifies on cooling. If any atmospheric air is mixed with the chlorine, a certain quantity of silica remains behind. (Berzelius.)—2. Dry chlorine gas is passed over a strongly ignited mixture of silica and charcoal. (Oerstedt, *Sch.* 26.) The heat required for this operation is stronger than that which an argand spirit-lamp can furnish. (Wöhler.) The yellow liquid obtained must be freed from the

excess of chlorine by agitation with mercury and distillation. (Dumas, *Ann. Chim. Phys.* 33, 267.)

Transparent and colourless liquid, having the appearance of ether. (Dumas.)—Heavier than water, but lighter than oil of vitriol; not freezing at − 20°; boiling at 50°. (Serullas, *J. Chim. Med.* 8, 3.) When exposed to the air, it evaporates almost instantaneously in the form of a white cloud, leaving a residue of silica. Its vapour has a suffocating odour, somewhat like that of cyanogen, and reddens litmus paper. (Berzelius.)

| | Calculation. | | | | Vol. | | Sp. gr. |
|---|---|---|---|---|---|---|---|
| Si | 15·0 | .... | 17·48 | Silicium vapour (?) | 1 | .... | 1·0400 |
| 2Cl | 70·8 | .... | 82·52 | Chlorine gas | 2 | .... | 4·9086 |
| $SiCl^2$ | 85·8 | .... | 100·00 | | 1 | .... | 5·9486 |

Chloride of silicium when thrown on water swims on its surface at first, and then dissolves in the form of hydrochlorate of silica. If the water is in excess, only a small quantity of silica is precipitated; but if the volumes of the two liquids are equal, a bulky mass of gelatinous silica is immediately produced. (Berzelius.) Oil of vitriol likewise resolves chloride of silicium into silica and hydrochloric acid. (Serullas.) Potassium heated in vapour of chloride of silicium, burns and forms chloride of potassium, with separation of silicium. (Berzelius.) Fused potassium dropped into liquid chloride of silicium, causes an explosion. Chloride of silicium may be heated over potassium till it boils, without undergoing decomposition; doubtless, because the boiling point of chloride of silicium is below the temperature at which potassium fuses. (Serullas.)

B. Hydrochlorate of Silica.—Obtained in the same manner as the sulphate, or by dissolving chloride of silicium in water. As fast as the acid escapes in the evaporation of this solution, the silica is deposited in the gelatinous state.

¶—C. Chlorosulphide of Silicium.—*Chlorosulphure de Silicium.*—Discovered by Isidore Pierre (*Ann. Pharm.* 69, 73), and formed by passing a mixture of vapour of chloride of silicium and perfectly dry hydrosulphuric acid gas through a red-hot porcelain tube. A large quantity of hydrochloric acid is formed, and escapes, together with the excess of chloride of silicium and traces of undecomposed hydrosulphuric acid. The best mode of preparation is to pass a current of hydrosulphuric acid gas through chloride of silicium contained in a stoppered retort, the conducting tube being made to dip just under the surface of the liquid. The retort is then connected by means of a good cork with one end of a porcelain tube, the other end of which is attached to a U-shaped tube kept constantly cool. The porcelain tube is then made red-hot, and as the mixture passes through, a fuming liquid rapidly condenses in the U-tube. The liquid thus obtained has a pungent, offensive odour resembling both chloride of silicium and hydrosulphuric acid; it becomes clear on standing, and is then distilled, the liquid which comes over at a temperature between 90° and 100° being kept apart. The process is stopped as soon as the pasty mass in the retort begins to evolve white fumes. The distillate is a colourless, transparent, watery liquid, which boils at 100°, and distils over without residue; its specific gravity is 1·45. In contact with water, it is decomposed, yielding hydrosulphuric acid gas, hydrochloric acid, silica, and a small quantity of free sulphur.

| | Calculation. | | Pierre. |
|---|---|---|---|
| Si ..... | 21·34 .... | 19·70 .... | 19·54 |
| S ..... | 16·00 .... | 14·82 .... | 15·01 |
| 2Cl ..... | 70·80 .... | 65·47 .... | 65·79 |
| $SiSCl^2$ .... | 108·14 .... | 100·00 .... | 100·34 |

The density of the vapour was found, in three experiments, to be 4·78, 5·24, and 5·23. The calculated density, supposing it condensed to three volumes, is 5·00.

## Silicium and Fluorine.

A. Fluoride of Silicium.—*Gaseous Fluoride of Silicium, Fluorspar gas, Hydrofluoric acid gas, Hydro-fluosilicic acid gas, Fluorkiesel, Fluorkiesel gas, Flussäure-kieselerde gas, Gaz acide fluorique, Gaz fluorique silicé.*—Formed on bringing hydrofluoric acid in contact with silica or any siliceous substance, such as glass. Anhydrous hydrofluoric acid becomes heated in contact with glass, boils up, and evolves gaseous fluoride of silicium.—The process of etching on glass with hydrofluoric acid depends on the formation of fluoride of silicium, when dilute hydrofluoric acid or the vapour of that acid, is made to act upon glass.

*Preparation.*—Powdered fluor-spar mixed with sand or finely pounded glass, is gently heated in a flask with oil of vitriol, and the gas collected over mercury in glass jars dried by heat. If the receivers are covered with the least film of moisture, they become overcast with an opaque deposit of silica, which cannot again be removed. (Berzelius.)

*Properties.* Colourless gas. Specific gravity (I., 280). It has a peculiarly penetrating and suffocating odour, like that of hydrochloric acid gas. According to J. Davy, it reddens litmus paper even when carefully dried. Forms a white cloud on exposure to the air. It is incombustible, and does not support the combustion of a taper or of burning wood.

| | Calculation. | | | Vol. | Sp. gr. |
|---|---|---|---|---|---|
| Si ..... | 15·0 .... | 28·63 | Vapour of silicium (?).... | 1 .... | 1·0400 |
| 2F ..... | 37·4 .... | 71·37 | Fluorine gas (?) ..... | 2 .... | 2·5928 |
| $SiF^2$ .... | 52·4 .... | 100·00 | Fluor. silic. gas ..... | 1 .... | 3·6328 |

| Or: | | | J. Davy. | | Berzelius. | |
|---|---|---|---|---|---|---|
| $SiO^2$ ..... | 31·0 .... | 59·16 | 61·4 .... | 59·1 | to | 58·976 |
| 2(F—O) .... | 21·4 .... | 40·84 | 38·6 .... | 40·9 | „ | 41·024 |
| $SiF^2$ ..... | 52·4 .... | 100·00 | 100·0 .... | 100·0 | „ | 100·000 |

F—O denotes hypothetically anhydrous fluoric acid.

*Decompositions.*—1. Water absorbs the gas in large quantity, and at the same time decomposes it, the products being hydrofluoric acid and silica; one-third of the latter is precipitated as a hydrate in white bulky flakes, whereby the liquid is soon converted into a thick, transparent, gelatinous paste, which fumes in the air; the rest forms ter-hydrofluate of silica, which remains dissolved in the water. (Berzelius.)

$$3SiF^2 + 6HO = 2SiO^2, 3HF + SiO^2.$$

The water absorbs the first quantities of gas rapidly; but after it has become thickened by the precipitated hydrate of silica, the absorption is

much slower. In 24 hours, 100 parts of water, in contact with an excess of gaseous fluoride of silicium, absorb 140·6 parts. (Berzelius.) 100 : 140·6 = 108 : 151·8; 108 represents 12 atoms of water; 151·8 is nearly 3 atoms of fluoride of silicium: hence 3 atoms of fluoride of silicium react on 6 atoms of water; and 6 other atoms of water remain partly combined with the free silica as hydrate, and partly with the ter-hydrofluate of silica, without any further power of decomposing the fluoride of silicium. The gelatinous mixture is probably : 2 (HO, HF + $SiO^2$, 2HF + Aq) + $SiO^2$, 2HO. According to J. Davy, one measure of water absorbs 265 measures of gaseous fluoride of silicium; this gives 134 parts of fluoride of silicium to 108 parts of water. The precipitated hydrate of silica is somewhat soluble in water; and consequently, the silica, after washing, amounts to only about $\frac{1}{4}$ instead of $\frac{1}{3}$ of the total amount of silica produced from the fluoride of silicium. When thoroughly washed, it is quite free from fluorine. The acid solution filtered from the hydrate of silica without having any additional water passed through it, yields, when saturated with potash, nothing but double fluoride of silicium and potassium. But if the solution is mixed with the subsequent washings, which contain a portion of the precipitated hydrate of silica in solution, the liquid, after saturation with potash, gelatinizes on being evaporated, in consequence of the excess of silica which it contains. (Berzelius.)—If hydrochloric acid gas is passed into water saturated with fluoride of silicium, the gelatinous condition is destroyed; a solution of hydrochloric acid is formed, and the silica disappears in the form of gaseous fluoride of silicium. (J. Davy.)

2. Gaseous fluoride of silicium is slowly absorbed by crystallized, but not by anhydrous boracic acid. The acid increases in bulk, and is converted into a white powder, which does not fume. 100 parts (2 atoms) of crystallized boracic acid absorb 129·02 parts (3 atoms) of fluoride of silicium. (Berzelius.)

$$2(BO^3, 3HO) + 3SiF^2 = 2(BO^3, 3HF) + 3SiO^2.$$

From this it appears that 2 atoms of terhydrofluate of boracic acid and 3 atoms of silica are produced.—The powder does not at first absorb water; but subsequently, a slight elevation of temperature takes place and terhydrofluate of boracic acid is dissolved, leaving a residue of hydrate of silica. About one-fourth, however, of the silica dissolves, and is again thrown down by ammonia and other bases. The residual portion of silica evolves pungent vapours when ignited, and may, with great probability, be regarded as another double salt containing excess of silica. (Berzelius.)

3. Aqueous solutions of salifiable bases either act like water, precipitating only one-third of the silica, and forming a double fluoride of silicium and the metal—as in the case of potassium—or they precipitate the whole of the silica and produce a simple fluoride of the metal, as in the case of sodium.

4. Many of the alkalis, earths, and heavy metallic oxides, in the anhydrous state, absorb gaseous fluoride of silicium, producing heat and sometimes even flame, and apparently forming a mixture of silica and metallic fluoride. Burnt lime, immersed in the gas, becomes red-hot through its whole mass (if moisture be present, the application of heat is necessary to commence the act of combination; an admixture of carbonate of lime likewise interferes with the action); and there is formed —without any evolution of oxygen gas—a tasteless mass, which is insoluble

in water, and when heated in the blowpipe flame, exhibits a bluish white phosphorescence, and cakes together into an anhydrous mass, hard enough to scratch glass. Hydrochloric acid slowly resolves this substance into soluble fluoride of calcium, and gelatinous silica which remains undissolved. With oil of vitriol it effervesces violently, evolving fluoride of silicium, and leaving a residue of gypsum, which amounts to 12·37 per cent. Hence it contains 2 atoms of lime to 1 atom of fluoride of silicium. (J. Davy.) [Or 2 atoms of fluoride of calcium to 1 atom of silica: $2CaO + SiF^2 = 2CaF + SiO^2$. Davy's view is supported by the fact that the silica, after treatment with hydrochloric acid, remains in the form of a hydrate: this, however, may likewise be explained by supposing that the silica is chemically combined with the fluoride of calcium.]—Baryta and alumina likewise absorb gaseous fluoride of silicium, but in smaller quantity, and again evolve it on the addition of oil of vitriol.—Magnesia likewise combines with it without ignition, and yields before the blowpipe an infusible mass, which resists the action of water, and behaves with hydrochloric and sulphuric acids in the same manner as the calcium compound.—The manganic, antimonic, mercuric, and ferric oxides likewise absorb a portion of gas—the latter most abundantly; the gas is again expelled by oil of vitriol. (J. Davy.)—Gaseous fluoride of silicium, passed over heated baryta, becomes red-hot, and is rapidly absorbed, in the proportion of 85·62 parts (4 atoms) of baryta to 14·38 parts (1 atom) of fluoride of silicium. (Dumas.)

$4BaO + SiF^2 = 2BaO, SiO^2 + 2BaF$; [the result is therefore a mixture of one atom of disilicate of baryta and 2 atoms of fluoride of barium.]—Anhydrous alkaline carbonates and salts of boracic acid do not act on gaseous fluoride of silicium at ordinary temperatures. (Berzelius.)

5. Potassium at ordinary temperatures acts slightly on gaseous fluoride of silicium; when heated in the gas till it fuses, it blackens and burns with a dark-red flame, absorbing a quantity of the gas equal in volume to the hydrogen which it would have evolved with water, and yielding a dark-brown, brittle mass. (Gay-Lussac & Thénard.) The potassium, on being heated, becomes first white, then darker, and lastly black, when it immediately takes fire. The resulting hard porous mass is a mixture of fluoride of potassium, double fluoride of silicium and potassium, and silicide of potassium. Water dissolves out potash and fluoride of potassium with violent evolution of hydrogen gas; on boiling, it also dissolves out double fluoride of silicium and potassium, and leaves silicium containing hydrogen, together with silica. (Berzelius.) Sodium produces similar results. (Gay-Lussac & Thénard.)—6. When the gas is passed through a white-hot gun-barrel filled with iron-turnings, very little is absorbed, the iron becoming covered with a thin stratum of silicium and fluoride of iron, which prevents any further action. On dissolving the fluoride of iron in water, a thin layer of silicium is left behind. (Berzelius.)—The following substances exert no decomposing action on gaseous fluoride of silicium: hydrogen gas in the direct rays of the sun, charcoal ignited in the gas; phosphorus, sulphur, or iodine sublimed in it; chloride of calcium ignited in it; chlorate of potash or of zinc fused in it. (J. Davy.)

*Combinations.—a.* With nitric oxide and the oxygen-acids of nitrogen.

*b.* With ammonia.

*c.* With other metallic fluorides, producing the METALLIC FLUO-SILICIDES or SILICO-FLUORIDES. These compounds are obtained: 1. By dissolving either a pure or a hydrated metallic oxide or its carbonate (or in

the case of iron or zinc, the simple metal) in ter-hydrofluate of silica till the liquid is nearly saturated,—when, if the compound is not insoluble, it is separated on evaporating the liquid in a platinum vessel. If it gelatinizes from excess of silica, a small quantity of hydrofluoric acid is to be added, and this, on further evaporation, is volatilized with the silica in the form of fluoride of silicium.—2. Fluoride of silicium is brought in contact with another metallic fluoride (either dry or in solution)—which readily absorbs the gas,—or with a pure metallic oxide or its carbonate, slightly moistened with water: in the latter case, a portion of the silicium is separated in the form of silica.—In these double metallic fluorides, one atom of fluoride of silicium is invariably combined with one atom of the other metallic fluoride.—Hence, by digesting bi-hydrofluate of soda with silica, the acid reaction of the solution is changed into an alkaline reaction; because, together with the insoluble double fluoride of silicium and sodium, mono-hydrofluate of soda, which has an alkaline reaction, is likewise formed. (Berzelius.)

$$2(NaO, 2HF) + SiO^2 = NaF, SiF^2 + NaO, HF + 3HO.$$

The silico-fluorides redden litmus, and for the most part have an acid, bitter taste.—By prolonged ignition, they give up the whole of the fluoride of silicium, the other metallic fluoride remaining behind in a pure state. If they contain water, the gaseous fluoride of silicium, as it escapes, is accompanied by a white sublimate in the form of minute drops, which, by the application of heat, may be chased from place to place, and appears to consist of concentrated *bi-hydrofluate of silica;* on exposure to moist air, it deposits silica. The silico-fluorides, many of them at least, are resolved by ignition with potassium into silicium and fluoride of potassium; whilst the other metallic fluoride previously in combination with the fluoride of silicium, either remains unaltered, or likewise gives up its fluorine to the potassium. The action of iron at a red heat is similar to that of potassium. (Berzelius.)—With oil of vitriol, the silico-fluorides at first evolve gaseous fluoride of silicium, which escapes with effervescence; then, at a temperature, which, in the case of the calcium and barium compound, exceeds 100°, anhydrous hydrofluoric acid is evolved. Hydrochloric and nitric acids expel only a part of the hydro-fluosilicic acid. On the other hand, the salts of nitric and hydrochloric acid are but imperfectly decomposed by hydro-fluosilicic acid. Hydrofluoric acid in excess does not affect them, but passes off unchanged on the application of heat. An alkali added to the aqueous solution of a metallic silico-fluoride, decomposes the fluoride of silicium in the compound on boiling—absorbing the fluorine and precipitating silica, *e. g.*

$$NaF, SiF^2 + 2NaO = 3NaF + SiO^2;$$

or, if we suppose that the metallic silico-fluoride is converted by water into a double hydrofluate of silica and another metallic oxide,

$$(NaO, HF + SiO^2, 2HF) + 2NaO = 3(NaO, HF) + SiO^2.$$

From the salts of the more soluble alkalis, the silica is thrown down pure; when precipitated from salts of the alkaline earths, it is mixed with fluoride of barium, strontium, or calcium; and from the salts of the earths and heavy metallic oxides (inasmuch as the alkaline precipitant likewise separates the hydrofluoric acid from these oxides) it is precipitated in a state of chemical combination with the bases, forming a simple silicate, *e. g.*

$$MgF, SiF^2 + 3NaO = MgO, SiO^2 + 3NaF;$$

or: $(MgO, HF + SiO^2, 2HF) + 3NaO = MgO, SiO^2 + 3(NaO, HF).$

Even when ammonia is the precipitating alkali and the second base of the double salt is soluble in it, a certain quantity of this base is still precipitated with the silica. (Berzelius.) The alkaline carbonates likewise decompose the metallic silico-fluorides, with effervescence, at a boiling heat. (Berzelius, H. Rose.)

*Hydrated Metallic Silico-fluorides or Compounds of Hydrofluate of Silica with Hydrofluates of other Metallic Oxides.*—Most silico-fluorides are easily soluble in water; only those of potassium, sodium, lithium, barium, calcium, and yttrium are sparingly soluble. (Berzelius.) The solution frequently yields hydrated crystals. Many of these crystals, when exposed to the air, lose their water of crystallization by efflorescence; and all of them undergo this change when heated.

B. Ter-hydrofluate of Silica.—*Hydro-fluosilicic acid, Kieselfluorwasserstoffsäure, Kieselhaltige Flussspathsäure, Acide fluorique sousilicé.*—Known only in combination with water.—Formed in the decomposition of fluoride of silicium by water (III., 362), and by dissolving silica in dilute hydrofluoric acid.—*Preparation.* A perfectly dry and intimate mixture of 4 parts of fluor-spar, and from 2 to 3 parts of quartz-sand or pounded glass, is put into a retort, and 5 parts of oil of vitriol poured over it; the whole is then well mixed together by shaking the retort, which should not be more than half full at the utmost. Heat is then very slowly applied, and increased towards the end of the experiment nearly to redness; the gaseous product is made to pass into water. As a narrow tube, if used for conveying the gas into the water, would soon become choked up with silica, one of the four following methods is adopted: *a.* The neck of the retort is attached to a tube bent at right angles, and having its lower end dipping under mercury. (Thénard.) Great care is necessary to prevent any water from getting into the tube above the mercury, and the mixture of fluor-spar and sand must be dried by heat; the oil of vitriol also should not contain more than one atom of water to one atom of sulphuric acid.—*b.* A wide and very short tube is adapted, by means of a cork, to the neck of the retort; and to its other end is attached the narrow opening of the neck of a broken receiver, the broad end of which reaches nearly to the bottom of an earthenware jar one-fourth filled with water. (Gmelin.)—*c.* The neck of the retort is connected with a bent tube which passes into a large bottle, one-fourth filled with water, without touching the liquid, and the absorption is promoted by frequent agitation. (Berzelius.)—*d.* The long neck of the retort is fitted into a long-necked receiver partly filled with water, and the receiver frequently shaken in order to keep its sides constantly wet. There is no escape of gas, and the silica is deposited in the form of a heavy crust from which the solution is easily filtered. (Maus, *Pogg.* 11, 86.)—The mixture of aqueous acid and gelatinous silica is thrown upon a linen strainer and the liquid pressed out. If the silica is exhausted with water, more hydro-fluosilicic acid is obtained, but mixed with an excess of silica, in consequence of the water dissolving a portion of the hydrate of silica. (Berzelius.)—2. Rock-crystal in powder may be thrown into artificially cooled hydrofluoric acid diluted with from 2 to 3 parts of water, till the acid is saturated, and the solution poured off from the insoluble residue. The silica dissolves quietly at first; but afterwards, if the rock-crystal is in excess and the acid concentrated, gaseous fluoride of silicium is evolved. (Berzelius.)—The acid thus obtained may be preserved in glass vessels. (J. Davy, Berzelius.)

Hydrofluosilicic acid has a very sour taste resembling that of hydrochloric acid, and, like that acid, irritates the skin; it reddens litmus strongly.

| | Calculation, *a*. | | | | Calculation, *b*. | | |
|---|---|---|---|---|---|---|---|
| HF | 19·7 | .... | 27·32 | $SiO^2$ | 31·0 | .... | 34·41 |
| $SiF^2$ | 52·4 | .... | 72·68 | 3HF | 59·1 | .... | 65·59 |
| $HF, SiF^2$ | 72·1 | .... | 100·00 | $SiO^2, 3HF$ | 90·1 | .... | 100·00 |

| | Calculation, *c*. | | |
|---|---|---|---|
| HO, HF | 28·7 | .... | 28·96 |
| $SiO^2$, 2HF | 70·4 | .... | 71·04 |
| HO, HF, $SiO^2$, 2HF | 99·1 | .... | 100·00 |

In calculation *a*, the hydro-fluosilicic acid is regarded as a metallic silico-fluoride, in which the atom of metal is replaced by an atom of hydrogen; in calculation *b*, as ter-hydrofluate of silica; in calculation *c*, it is made to correspond to a hydrated metallic silico-fluoride, supposing that the latter compound forms with water a double hydrofluate of silica and a metallic oxide, *e. g.*

$$KF, SiF^2 + 3HO = KO, HF + SiO^2, 2HF.$$

In that case, we must suppose that in hydro-fluosilicic acid, the metallic oxide (KO) is replaced by HO. But the hydro-fluosilicic acid cannot be obtained in the anhydrous state assumed in the calculations *a*, *b*, and *c*. The most concentrated acid that can be prepared is still combined, according to Berzelius, with 3 atoms of water more than that which exists according to calculation *c*: $HO, HF + SiO^2\ 2HF + 3Aq$.

Hydro-fluosilicic acid gradually evaporates at a temperature of 40° without leaving any residue; if evaporated on glass, it corrodes the surface; for, fluoride of silicium is evolved at first, and the residual liquid becomes stronger and stronger in hydrofluoric acid, which subsequently evaporates also. Hence the acid attacks glass when evaporated upon it, but not when it is preserved in stoppered glass bottles. When evaporated in vacuo over oil of vitriol, it likewise corrodes the glass receiver; because, after the fluoride of silicium has been evolved, a compound richer in hydrofluoric acid remains and is gradually evaporated. Berzelius.)—Boracic acid precipitates silica from the solution and forms ter-hydrofluate of boracic acid. (J. Davy.)

$$SiO^2, 3HF + BO^3 = BO^3, 3HF + SiO^2.$$

—Oil of vitriol, or hydrochloric acid gas, absorbs water from the compound and liberates gaseous fluoride of silicium. (J. Davy.)—An excess of ammonia or soda (and of most other salifiable bases: Berzelius) gives rise to the formation of a hydrofluate, and separates the whole of the silica. (J. Davy.)—Salts of ammonia, potash, and soda produce a transparent, gelatinous precipitate, scarcely perceptible at first; those of baryta, a white crystalline precipitate, which becomes visible after a few seconds. From many other salts, likewise, hydro-fluosilicic acid throws down a silico-fluoride of the metal. (Berzelius.)

Concentrated hydro-fluosilicic acid exposed to the air at ordinary temperatures, absorbs moisture till it reaches a certain degree of dilution; a very dilute acid, on the contrary, gives off water in the air till it attains the same degree of concentration. (Berzelius.)

## Silicium and Nitrogen.

A. Nitrate of Silica.—Prepared like the hydrochlorate.

B. Silicate of Ammonia.—Pure liquid ammonia dissolves a tolerably large quantity of freshly precipitated silica; the carbonate dissolves it but very sparingly. (Karsten, *Pogg.* 6, 357.)

C. Ammonio-Chloride of Silicium.—Formed by saturating chloride of silicium with dry ammoniacal gas.—White mass, resisting the action of fire, but decomposed by water. (Persoz, *Ann. Chim. Phys.* 44, 319.)

$$3NH^3, SiCl^2 + 2HO = 2(NH^3, HCl) + SiO^2 + NH^3.$$

| | Calculation. | | Persoz. |
|---|---|---|---|
| $3NH^3$ | 51·0 | 37·28 | 37·559 |
| $SiCl^2$ | 85·8 | 62·72 | 62·441 |
| $3NH^3, SiCl^2$ | 136·8 | 100·00 | 100·000 |

D. Fluoride of Silicium is capable of uniting with *nitric oxide, nitrous acid, hyponitric acid,* and *nitric acid.* Monohydrated nitric acid ($HO, NO^5$) absorbs gaseous fluoride of silicium greedily, producing a fuming liquid from which neither water nor alkalis precipitate silica. (Kuhlmann, *Ann. Chim. Phys.* 77, 116; also *Ann. Pharm.* 39, 319.)

E. Ammonio-fluoride of Silicium.—One volume of gaseous fluoride of silicium condenses—in whatever proportions the two gases are mixed—with 2 measures of ammoniacal gas, forming a white powder which volatilizes without being decomposed. Carbonate of ammonia is likewise decomposed by fluoride of silicium at the temperature at which it volatilizes. The powder is resolved by hydrochloric acid gas into sal-ammoniac and gaseous fluoride of silicium. It dissolves in water, with separation of one-fourth of the silicium, yielding a solution of double hydrofluate of silica and ammonia. (J. Davy.)—

$$2(NH^3, SiF^2) + 4HO = (NH^3, HF + SiO^2, 2HF) + NH^3, HF + SiO^2.$$

Consequently half of the silica must be separated; and the solution must contain one atom of hydrofluate of ammonia in addition to one atom of the double hydrofluate of silica and ammonia.

| | Calculation. | | J. Davy. |
|---|---|---|---|
| $NH^3$ | 17·0 | 24·49 | 24·5 |
| $SiF^2$ | 52·4 | 75·51 | 75·5 |
| $NH^3, SiF^2$ | 69·4 | 100·00 | 100·0 |

F. Fluoride of Silicium and Ammonium and Hydrofluate of Silica and Ammonia.—1. An intimate mixture of sal-ammoniac and silico-fluoride of potassium or sodium is heated in a glass vessel till the compound sublimes. (Berzelius.)—2. Terhydrofluate of silica is neutralized with a dilute solution of ammonia. On neutralizing hydrofluosilicic acid with ammonia, a small quantity of silica is thrown down, and the mother-liquid still remaining in the crystalline mass contains pure hydrofluoric acid or bi-hydrofluate of ammonia. An excess of ammonia is to be avoided, as it would precipitate the silica still more completely. (Berzelius.) When the solution is evaporated spontaneously, the salt

crystallizes in large short, transparent, brilliant, four-sided (J. Davy), or six-sided (Berzelius) prisms, containing water of crystallization. The crystals decrepitate slightly when heated, and, without fusing or undergoing decomposition, sublime in a solid crystalline mass. (Berzelius.) The salt has a strong saline taste and reddens litmus. (J. Davy.)

Fluoride of Silicium and Ammonium.

| | | | |
|---|---|---|---|
| $NH^4F$ | 36·7 | ..... | 41·19 |
| $SiF^2$ | 52·4 | ..... | 58·81 |
| $NH^4F + SiF^2$ | 89·1 | ..... | 100·00 |

Hydrofluate of Silica and Ammonia.

| | | | |
|---|---|---|---|
| $NH^3, HF$ | 36·7 | ..... | 34·27 |
| $SiO^2, 2HF$ | 70·4 | ..... | 65·73 |
| $NH^3, HF + SiO^2, 2HF$ | 107·1 | ..... | 100·00 |

The amount of water contained in the crystalline compound has not yet been ascertained by experiment.

A solution of the salt boiled in glass vessels dissolves a portion of their silica, which is again thrown down on diluting with water. (J. Davy.)—Sulphuric acid decomposes the salt, with evolution of gaseous fluoride of silicium and of hydrofluoric acid; the action of hydrochloric acid gas is less energetic; and the concentrated aqueous acid does not affect it at all. (J. Davy.)—Potash liberates ammonia and forms fluoride of silicium and potassium, but does not precipitate silica; soda, according to J. Davy, acts in a similar manner to potassium; according to Gay-Lussac & Thénard, it precipitates the whole of the silica; ammonia forms hydrofluate of ammonia, and separates all the silica in the salt. (J. Davy.) According to Gay-Lussac & Thénard, and likewise according to Berzelius, a portion of silica remains dissolved in the aqueous solution. —The salt is very soluble in water, but does not deliquesce in the air. (J. Davy, Berzelius.)

### Silicium and Potassium.

A. Silicide of Potassium.—The two elements, when heated together, unite without perceptible incandescence. The compound containing a larger proportion of potassium than silicium is dark greyish-brown, and dissolves entirely in water, evolving hydrogen gas and yielding silicate of potash; the compound which contains more silicium than potassium—obtained by the decomposition of fluoride of silicium by potassium, and also by strongly igniting the first compound—leaves a residue of silicium when digested in water. (Berzelius.) When vapour of potassium is passed over ignited silica, silicate of potash and silicide of potassium are produced, and dissolve in water without leaving any residue. But if the greater part of the potassium be previously expelled at a strong red heat, and the remaining vitreous mass digested, first in water and then in hydrofluoric acid, a small quantity of silicium is left behind. (Berzelius.)

B. Silicate of Potash.—*a. Monosilicate.*—Silica fused with an excess of carbonate of potash expels a quantity of carbonic acid, the amount of oxygen in which is equal to that in the silica itself. (H. Rose, *Gilb.* 73, 84.) Consequently, one atom of $SiO^2$ expels one atom of $CO^2$.

The salt is formed by fusing 31 parts of silica with 69·2 parts of carbonate of potash (= 1 part : 2¼ parts).—Transparent and colourless glass which deliquesces in the air.

| | | Calculation. | |
|---|---|---|---|
| KO ..... | 47·2 | ..... | 60·36 |
| $SiO^2$ ..... | 31·0 | ..... | 39·64 |
| KO, $SiO^2$ ..... | 78·2 | ..... | 100·00 |

Berzelius fused 1 part of silica with 4 parts of hydrate of potash; slowly cooled the mixture till one-half solidified; and then poured off the remaining liquid. Pearly crystals of silicate of potash were obtained in this manner, but their composition is not stated.

*b. Hydrated.—Kieselfeuchtigkeit, Liquor Silicum.*—1. By dissolving the fused compound in water.—2. By dissolving silica in solution of caustic potash. Freshly precipitated, unignited silica dissolves even in a cold aqueous solution of potash, with evolution of heat; artificially prepared silica, after strong ignition, also dissolves completely but slowly in a cold solution, and rapidly in a boiling solution of potash. The different kinds of opal behave like precipitated silica; of all the varieties, hyalite dissolves the most slowly in a cold solution of potash. Quartz, even in a state of minute division, is perfectly insoluble in a cold solution, and dissolves but very slowly and with great difficulty in a boiling solution of potash. (Fuchs, *Schw.* 24, 378; 67, 418.) When pounded rock-crystal is boiled to dryness with three several quantities of potash-ley (till, in fact, nothing but hydrate of potash remains) solution is effected. (Löwitz, *Crell. Ann.* 1799, 2, 375.) Glass likewise dissolves with various degrees of readiness in a hot solution of potash, yielding a similar liquid.

The silica-solution is transparent (unless accidentally rendered turbid by the presence of silicate of lime, &c.); has a strong alkaline taste and reaction; and is corrosive.—Acids separate the potash from it. According to Dalton, the addition of an acid in quantity not sufficient for saturation, precipitates a compound of the potash with excess of silica; a larger quantity throws down the silica in the form of a gelatinous hydrate, leaving in solution a quantity of silica, which is greater in proportion to the degree of dilution and to the excess of acid employed. ¶ According to Doveri (*N. Ann. Chim. Phys.* 21, 40), an excess of acid added drop by drop to a solution of silicate of potash, of density between 36° and 24° Baumé, precipitates $\frac{9}{16}$ of the silicic acid; from a solution of 8° B., $\frac{4}{16}$ are precipitated, while a solution of 6° B. retains the whole of the silica. If the acid be added at once and not in drops, or if the silica solution be added to the acid, no precipitate is obtained, even in concentrated solutions. But the addition of chloride of potassium to the solution of 6° B. renders it capable of being precipitated by hydrochloric acid. The silica appears to combine with the acid at the moment of liberation; for on neutralizing the acid with potash added drop by drop, the whole of the silica is precipitated. Carbonic acid and alkaline bicarbonates precipitate silica from the solution, so that the mixture assumes a pasty consistence, resembling coagulated albumen; the precipitate is insoluble in acids. ¶ From a concentrated solution of silica, acids immediately precipitate gelatinous silica, which afterwards dissolves with great difficulty and only in excess of the acid.—If to a dilute solution of silica in potash, containing at least $\frac{1}{30}$ of silica, a quantity of acid be added sufficient only to neutralize the potash, the mixture at first continues clear; but, according to Bergman (*Opusc.* 3, 315), becomes turbid immediately on boiling, and slowly

at ordinary temperatures, with separation of viscid flakes which are not dissolved on a further addition of acid. (Karsten.) A dilute silica-solution supersaturated with sulphuric, hydrochloric, nitric, or acetic acid remains clear, even after long standing or exposure to heat, or when nitre and other salts are dissolved in it; and it is only by evaporation that a precipitate of gelatinous silica can be obtained from it.—If a dilute solution of silica be first supersaturated with hydrochloric acid and then mixed in a close vessel with enough carbonate of ammonia to neutralize all the hydrochloric acid, so that free carbonic acid alone remains in the liquid, the silica is held in solution by the latter, but separates on exposing the liquid to the air or on heating it, in consequence of the evolution of carbonic acid. (Karsten, *Pogg.* 6, 357.)—Solution of silica exposed to the air absorbs carbonic acid and is converted, in the course of a fortnight, into a transparent jelly which gradually shrinks together, and after some months becomes hard enough to scratch glass. It is probable that opal and flint are formed in a similar manner; at all events, potash enters into their composition. (Kuhlmann, *Ann. Pharm.* 41, 231.) The ammoniacal salts also precipitate solution of silica, their acid neutralizing the potash and the ammonia being set free.—Baryta, strontia, and lime-water, and likewise alumina dissolved in solution of potash, throw down the whole of the silica, together with part of the potash, in the form of a double silicate, the rest of the potash remaining in the liquid in the free state. (Guyton Morveau, *Ann. Chim.* 31, 246; Bucholz, *Taschenb.* 1812, 156; Döbereiner, *Schw.* 10, 113.)

*b. Bisilicate.*—If a solution of precipitated silica in excess of boiling potash, is mixed with about half its volume of alcohol, a solution of bisilicate of potash separates, and forms a distinct stratum beneath the alcoholic solution. The latter is poured off; the heavier stratum diluted with water; again precipitated with alcohol and left in contact with that liquid for the space of twenty-four hours. The transparent liquid beneath is then covered with a thin stratum of carbonate of potash, and lastly with alcohol, from which it is separated by a syphon. (Forchhammer, *Pogg.* 35, 339.)

| | Anhydrous. | | | | Forchammer. |
|---|---|---|---|---|---|
| KO ..... | 47·2 | .... | 43·22 | ..... | 44·77 |
| $2SiO^2$ ..... | 62·0 | .... | 56·78 | ..... | 55·23 |
| $KO, 2SiO^2$ ..... | 109·2 | .... | 100·00 | ..... | 100·00 |

*c. Tetrasilicate.—Soluble Glass* of Fuchs.—1. Fifteen parts of powdered quartz are ignited with 10 parts of crude potash and one part of charcoal, (which decomposes and expels the sulphuric acid contained in the potash) till perfect vitrification takes place. The hard, blistered, greyish-black glass thus obtained, is pulverized—then boiled with five times its weight of water (in which it dissolves slowly but almost entirely in the course of four hours)—and the solution finally evaporated. (Fuchs.) With a larger proportion of silica, or in presence of lime, alumina, &c., which form double salts, an insoluble glass is produced. (Fuchs.) Buchner (*Repert.* 46, 530; 51, 393) uses 6 parts of powdered quartz and 10 parts of half-refined tartar.—2. An aqueous solution of potash is saturated with freshly precipitated hydrate of silica and evaporated. (Fuchs.) In order to obtain the mass prepared by either of these methods, in the anhydrous state, it must be heated till it fuses. Hard, transparent, rather infusible glass, which, on exposure

to the air, absorbs so much water (without any external change, excepting that it becomes slightly fissured) that it swells up strongly when heated. (Fuchs.)

| | Calculation. | | Forchhammer. |
|---|---|---|---|
| KO | 47·2 | 27·57 | 28·43 |
| $4SiO^2$ | 124·0 | 72·43 | 71·57 |
| $KO, 4SiO^2$ | 171·2 | 100·00 | 100·00 |

*Hydrated.*—The substance obtained by simply drying the solution is colourless, transparent, and brittle, with a conchoidal, vitreous fracture, but softer than glass. It has a slightly alkaline taste and reaction, and after thorough drying, contains 26 per cent. of potash, 62 of silica, and 12 of water. The salt is permanent in the air; does not absorb carbonic acid from it; and effloresces only when accidentally mixed with other salts of potash. In the fire it swells up from loss of water, then fuses, and forms anhydrous soluble glass. Dilute acids decompose it, with separation of silica, more easily than concentrated acids. It dissolves but very slowly in cold, but readily in boiling water. (Fuchs.)

A concentrated solution containing 28 per cent. of anhydrous soluble glass, is syrupy, tenacious, somewhat turbid, and of specific gravity 1·25. On boiling or on exposure to the air, it becomes covered with a tough skin, which disappears when thrust beneath the liquid. After evaporation at a high temperature, it becomes very tenacious, and may be drawn out in threads, like melted glass. It dries up to a varnish when spread upon wood, &c., the combustibility of which it diminishes. A dilute solution absorbs carbonic acid from the air; a concentrated solution scarcely at all; it is decomposed, however, by a current of carbonic acid gas, and converted into a stiff jelly. The stronger acids precipitate silica from the solution. The alkaline carbonates and chlorides also—especially sal-ammoniac (and according to Persoz, acetate of soda)—precipitate the silica. Sal-ammoniac precipitates a dilute solution gradually, and a concentrated solution immediately, converting it into a tenacious mass. The precipitate is pasty at first, and, after long-continued washing, leaves pure silica. Baryta, strontia, lime, alumina, and oxide of lead combine with the whole of the silica and a portion of the potash, forming an insoluble compound. Nearly all the soluble salts of the earths and heavy metallic oxides, likewise produce a bulky precipitate. Phosphate of alumina, and carbonate, phosphate, or sulphate of lead, when rubbed up with a solution of soluble glass, yield a tenacious mass, which becomes as hard as stone in the air; phosphate of lime is not decomposed by it. Alcohol, even in small quantity, precipitates soluble glass from an aqueous solution, and thus affords the means of purifying it from other salts of potash. (Fuchs, *Kastn. Arch.* 5, 385.) The alcohol, however, withdraws potash—even in the precipitation of the salt, and still more on washing—until octosilicate of potash alone remains. (Forchhammer.)

*d. Potash-glass.*—*a.* One part of carbonate of potash fused with 2 parts of quartz-sand, yields a glass which is but partially soluble in water. *b.* With 3 parts of quartz-sand, an insoluble glass is obtained, which, however, is very refractory in the fire, and consequently difficult to work. (Fuchs, *Kastn. Arch.* 5, 396.) In *a*, one atom of potash is combined with about 4·5 atoms; in *b*, with about 7 atoms of silica.

*e. Octosilicate.*—An aqueous solution of soluble glass (tetrasilicate) is mixed with excess of alcohol, and the precipitate washed with al-

cohol of 30 per cent. till the alcohol which passes through is no longer alkaline. The hydrated residue is only partially soluble in hot water; *vid. seq.* (Forchhammer.)

| | Anhydrous. | | | Forchhammer. |
|---|---|---|---|---|
| KO | 47·2 | .... | 15·99 | 16·71 |
| $8SiO^2$ | 248·0 | .... | 84·01 | 83·29 |
| $KO, 8SiO^2$ | 295·2 | .... | 100·00 | 100·00 |

A mixture of one atom of potash with even 9 atoms of silica is still completely fusible at the heat of a blast-furnace; with 15 atoms of silica, the mass scarcely cakes together. (Mitscherlich.)

*f. With* 18 *atoms of Silica.*—On thoroughly boiling the octosilicate of potash in water, the tetrasilicate dissolves, and leaves a residue of hydrated octodeca-silicate of potash. (Forchhammer's analysis of the tetrasilicate (III. 372) was performed with the salt prepared by this method.)

| | Anhydrous. | | | Forchhammer. | | Hydrated. | | | Forchhammer. |
|---|---|---|---|---|---|---|---|---|---|
| KO | 47·2 | .... | 7·8 | 7·73 | KO | 47·2 | .... | 6·88 | 6·77 |
| $18SiO^2$ | 558·0 | .... | 92·2 | 92·27 | $18SiO^2$ | 558·0 | .... | 81·32 | 80·85 |
| | | | | | 9HO | 81·0 | .... | 11·80 | 12·38 |
| $KO, 18SiO^2$ | 605·2 | .... | 100·0 | 100·00 | +9Aq. | 686·2 | .... | 100·00 | 100·00 |

*g. With* 24 *atoms of Silica.*—This is the gelatinous precipitate which separates on cooling from a solution of silica in boiling carbonate of potash, thoroughly purified with water and dried in the air. (Forchhammer.)

| | Anhydrous. | | | | Dried in the air. | | | Forchhammer. |
|---|---|---|---|---|---|---|---|---|
| KO | 47·2 | .... | 5·96 | KO | 47·2 | .... | 5·05 | 4·61 |
| $24SiO^2$ | 744·0 | .... | 94·04 | $24SiO^2$ | 744·0 | .... | 79·55 | 79·26 |
| | | | | 16HO | 144·0 | .... | 15·40 | 16·13 |
| $KO, 24SiO^2$ | 791·2 | .... | 100·00 | +16Aq. | 935·2 | .... | 100·00 | 100·00 |

One measure of powdered charcoal or graphite heated to whiteness for three hours with 6 measures of silica containing a small quantity of potash, in a crucible covered with sand, yields a black glass, in which the eye cannot discover any black powder intermixed. But on dissolving the silica in hydrofluoric acid, the carbon is separated in a pulverulent form. (Prater, *Phil. Mag. J.* 20, 72.) [Probably a mere mixture.]

C. Carbonate of Silica and Potash.—A boiling aqueous solution of carbonate of potash dissolves the hydrate of silica, and likewise silica which has not been too strongly ignited, and deposits it again as an opalescent jelly on cooling. (Pfaff, *Schw.* 29, 383.) Powdered quartz is the least soluble. Opal and silica after ignition are more easily dissolved, and unignited silica most readily of all. (H. Rose.) The earth which separates on cooling retains $\frac{1}{24}$ At. potash. (Forchhammer.)

D. Sulphide of Silicium and Potassium.—Silicide of potassium is first heated with sulphur—whereupon the potassium becomes incandescent and combines with the sulphur—and the mass afterwards exposed to a white heat, at which temperature the potassium gives up a portion of sulphur to the silicium, and is itself reduced to a lower degree of sulphuration. The mass, before it has been heated to whiteness, dissolves

in water, with separation of a considerable quantity of silicium. Sulphide of silicium and potassium is blackish brown, and dissolves in water without residue, probably as silicate and hydrosulphate of potash. (Berzelius.)

E. Fluoride of Silicium and Potassium.—Silicium explodes with double fluoride of hydrogen and potassium at a temperature considerably below redness. When terhydrofluate of silica is added to an aqueous solution of potash, or of a potash-salt (in the latter case the acid of the salt is set free: *Scheele*), the double fluoride separates very slowly, and is at first scarcely visible; afterwards, it produces prismatic colours in the liquid, and is finally deposited as a transparent, gelatinous, iridescent mass. This mass dries upon the filter to a soft, white powder, which has an acid, bitter taste, and reddens litmus. By evaporating a saturated aqueous solution, the compound may also be obtained, in very small anhydrous crystals, having the form of the rhombohedron or the six-sided prism. (Berzelius.)

| | | Calculation. | |
|---|---|---|---|
| K | 39·2 | ..... | 35·54 |
| Si | 15·0 | ..... | 13·60 |
| 3F | 56·1 | ..... | 50·86 |
| $KF, SiF^2$ | 110·3 | ..... | 100·00 |

| Or: | Atoms. | | | | | | Berzelius. |
|---|---|---|---|---|---|---|---|
| Potash | 1 | .... | 47·2 | .... | 42·79 | .... | 42·634 |
| Silica | 1 | .... | 31·0 | .... | 28·11 | | |
| Hyp. anhydrous fluoric acid | 3 | .... | 32·1 | .... | 29.10 | | |
| | 1 | .... | 110·3 | .... | 100·00 | | |

Fluoride of silicium and potassium fuses at a low red-heat; at a higher temperature it boils, and slowly evolves gaseous fluoride of silicium, but continually becomes more and more refractory, till, after prolonged ignition, fluoride of potassium is left containing silica in solution, (because, when the process is performed in an open crucible, the aqueous vapour of the flame of the spirit-lamp separates a portion of silica from the fluoride of silicium). Heated with potassium, it is resolved into silicium and fluoride of potassium. Ignited with iron at a white heat, it yields a mixture of fluoride of potassium, fluoride of iron, and silicide of iron. When oil of vitriol is poured upon it, gaseous fluoride of silicium and hydrofluoric acid are evolved. It is only partially decomposed by digestion with aqueous solution of boracic acid; so that the quantity of the silica separated is very far short of the whole. It is not decomposed in the cold by a solution of caustic potash or carbonate of potash; but when it is boiled with the latter, carbonic acid is evolved and complete decomposition effected; on cooling, the separated silica is deposited in a gelatinous form, leaving hydrofluate of potash in solution. (Berzelius.) It removes every trace of lime from lime water. (Scheele.) It dissolves very sparingly in water, more freely, however, when the water is hot. (Scheele, Gay-Lussac & Thénard.)

F. Silicated Fluoride of Potassium.—Fluoride of potassium in a state of fusion unites with silica, forming a transparent, fused mass, which does not evolve fluoride of silicium at a rather strong red heat; but, on cooling, solidifies to a white enamel, which deliquesces in the air, and dissolves in water with separation of silica. (Berzelius.)

G. NITRIDE OF SILICIUM AND POTASSIUM (?)—A mixture of 6 parts of silica with 13 parts of cyanide of potassium, exposed for an hour in a closely covered crucible to the heat of a smith's forge, yields a porous glass which fuses tranquilly in the inner blowpipe flame, but with evolution of gas in the outer; and when heated with a mixture of hydrate of lime and carbonate of potash, evolves a large quantity of ammonia, even after being thoroughly washed with water or boiled with sulphuric acid. (Balmain, *Phil. Mag. J.* 21, 276; also *J. pr. Chem.* 27, 422.)

## SILICIUM AND SODIUM.

A. SILICATE OF SODA.—a. *Monosilicate.*—31 parts (1 At.) of silica fused with 53·2 parts (1 At.) of dry carbonate of soda, give off carbonic acid, and form a soluble glass resembling the glass of the silica-solution (*liquor silicum*).

*Hydrated.*—In an aqueous solution of soda, a quantity of silica is dissolved equal to the quantity of anhydrous soda present; the liquid is then evaporated and left to crystallize. A concentrated solution solidifies after some days to a crystalline mass; a more dilute solution deposits hemispherical, fibrous masses or a crystalline crust. The crystals sometimes contain 6 atoms, sometimes 9 atoms of water of crystallization. (Fritzsche.)

α. *Sexhydrated.*—Oblique rhomboidal prisms, belonging to the doubly oblique prismatic system. (Fritzsche.)

| | Crystallized. | | Fritzsche. |
|---|---|---|---|
| NaO | 31·2 | 26·85 | 26·8 |
| $SiO^2$ | 31·0 | 26·68 | 26·2 |
| 6HO | 54·0 | 46·47 | 47·0 |
| $NaO, SiO^2 + 6Aq.$ | 116·2 | 100·00 | 100·0 |

β. *Octohydrated.*—Crystallizes from the mother-liquid obtained in the purification of crude soda. White rhombs, permanent in the air, and having a caustic taste. The salt melts in its own water of crystallization, and leaves a white, swollen mass, which does not fuse over the flame of the spirit-lamp. Very soluble in water. (R. Hermann, *J. pr. Chem.* 12, 294.)

γ. *With 9 atoms of Water.*—Right rectangular prisms terminated with the four faces of a rhombic octohedron, together with four faces of a more acute rhombic octohedron. In a glass jar over oil of vitriol, the crystals effloresce throughout their whole mass. The salt attracts carbonic acid from the air without deliquescing. Fuses at 40°, and forms a syrupy liquid, which solidifies again, but not till after the lapse of some days. (Fritzsche, *Pogg.* 43, 135.)

| | β. | | Hermann. |
|---|---|---|---|
| NaO | 31·2 | 23·25 | 22·96 |
| $SiO^2$ | 31·0 | 23·10 | 22·67 |
| 8HO | 72·0 | 53·65 | 54·37 |
| $NaO, SiO^2 + 8Aq.$ | 134·2 | 100·00 | 100·00 |

| | γ. | | Fritzsche. |
|---|---|---|---|
| NaO | 31·2 | 21·79 | 21·86 |
| $SiO^2$ | 31·0 | 21·65 | 21·55 |
| 9HO | 81·0 | 56·56 | 56·59 |
| + 9Aq. | 143·2 | 100·00 | 100·00 |

*b. Five-halves Silicate of Soda.*—One part of quartz fused with 2 parts of crystallized carbonate of soda yields a soluble glass similar to the potash compound, and preferable to it for practical purposes. (Fuchs.) In this glass, 2·3 atoms of silica are combined with 1 atom of soda; but it likewise contains alumina derived from the earthen crucible: if a larger excess of silica were present, the alumina would render the glass insoluble.

*c. Tersilicate.*—*α.* 100 parts of quartz fused with 40 parts of hydrate of soda, and rapidly cooled, yield a pellucid glass; but if very slowly cooled, a brownish glass with crystalline points. Both varieties contain 21·6 per cent. of soda, 2·0 of alumina (from the crucible), and 76·4 of silica. (Dumas.)

*β.* The glass obtained by fusing 3 parts of powdered quartz with 2 parts of dry carbonate of soda in a platinum crucible, is reduced to powder —washed with cold water—and afterwards boiled for a long time with the same liquid. The solution thus obtained is mixed with alcohol in such quantities, that the mixture may contain 30 per cent. of absolute alcohol. A white precipitate is then thrown down, and is purified by pouring off the spirituous liquid, dissolving in water, and re-precipitating by means of alcohol. The white precipitate dries up to a transparent varnish, still containing water. The same compound is found in the water of the Geiser springs. (Forchhammer, *Pogg.* 35, 343.)

| | Anhydrous. | | | | Forchhammer. |
|---|---|---|---|---|---|
| NaO ..... | 31·2 | .... | 25·12 | .... | 26·047 |
| $SiO^2$ ..... | 93·0 | .... | 74·88 | .... | 73·953 |
| $NaO, 3SiO^2$ .... | 124·2 | .... | 100·00 | .... | 100·000 |

*d. Tetrasilicate.*—The boiling mother-liquor is saturated with artificially prepared and unignited silica, and the alkaline filtrate evaporated to dryness. It becomes more and more tough, and when dried at a temperature of 117° (242·6° F.) leaves a pale yellow, transparent glass. This, on ignition, loses water and swells up to a spongy mass, which is infusible in the blowpipe flame, and does not absorb moisture from the air. The vitreous mass, before ignition, absorbs water from the air, and dissolves very slowly in water. A solution so far diluted as to contain only from $\frac{1}{10}$ to $\frac{1}{40}$ part of silica, solidifies immediately when exactly neutralized with an acid, and forms a solid transparent jelly. With $\frac{1}{50}$ to $\frac{1}{100}$ part of silica it does not form a jelly till after the lapse of twelve hours; with $\frac{1}{300}$ part of silica, no reaction takes place. The slightest excess of acid prevents the formation of the jelly. If a current of carbonic acid gas be passed through a solution containing $\frac{1}{100}$ part of silica, no jelly is formed till the liquid has been boiled or exposed to the air. With sulphate or hydrochlorate of ammonia, a solution of the above strength forms a jelly after a few minutes; a solution containing $\frac{1}{300}$ to $\frac{1}{1000}$ part of silica, deposits a few flakes in the course of 24 hours. (A. J. Walcker, *N. Quart. J. of Sc.* 3. 371.)

| | In the vitreous state. | | | | Walcker. |
|---|---|---|---|---|---|
| NaO ..... | 31·2 | .... | 11·86 | .... | 11·76 |
| $4SiO^2$ ..... | 124·0 | .... | 47·11 | .... | 45·71 |
| 12HO ..... | 108·0 | .... | 41·03 | .... | 42·53 |
| $NaO\ 4SiO^2 + 12Aq.$ .... | 263·2 | .... | 100·00 | .... | 100·00 |

One atom of soda may be fused with 9 atoms of silica in a blast-furnace; with 15 atoms it merely forms a caked, semi-vitrefied mass. (Mitscherlich.)

*e. With 36 atoms of Silica.*—Freshly precipitated silica is dissolved in a boiling concentrated solution of carbonate of soda; the solution filtered; and the precipitate which forms on cooling, thoroughly washed with boiling water. (Forchhammer, *Pogg.* 35, 343.)

| | Ignited. | | Forchhammer. |
|---|---|---|---|
| NaO | 31·2 | 2·72 | 2·74 |
| $36SiO^2$ | 1116·0 | 97·28 | 97·26 |
| $NaO, 36SiO^2$ | 1147·2 | 100·00 | 100·00 |

| | Dried in vacuo. | | Forchhammer. |
|---|---|---|---|
| NaO | 31·2 | 2·64 | 96·37 |
| $36SiO^2$ | 1116·0 | 94·32 | |
| 4HO | 36·0 | 3·04 | 3·63 |
| + 4Aq. | 1183·2 | 100·00 | 100·00 |

## *Glass.*

*Glass* is a mixture of silicate of potash or soda, or of both, with one or more silicates insoluble in water, as silicate of baryta, strontia, lime, magnesia, alumina, protoxide of manganese, protoxide of iron, sesquioxide of iron, and oxide of lead. Pure silicate of potash or soda, or a mixture of the two, even with a sufficient quantity of silica to form a very infusible glass, would still be attacked by water and acids. Silicate of lime is likewise acted on by acids; but a mixture of it with silicate of potash or soda resists their action. Such mixtures of silicate of soda or potash with silicate of lime, &c., are more fusible than the simple salts, and require a smaller amount of silica to render them capable of resisting the action of water and of acids. They contain between 2 and 3 atoms of silica to 1 atom of base, and still less when alumina is also present. The glass is more infusible, and offers greater resistance to the action of water and of acids, the larger the proportion of silica and alumina it contains; it is more easily fused and attacked by water and acids, the greater the excess of potash, soda, baryta, lime, magnesia, or oxide of lead which it contains; an excess of the last-mentioned oxide renders it particularly fusible, of a high specific gravity, soft, easily scratched, and corroded by acids. According to Baudrimont & Pelouze (*J. Chim. Med.* 9, 277), the lustre and refractive power of glass increase with the atomic weight of the bases contained in it; thus, these qualities are possessed in the highest degree by lead-glass, next by baryta-glass, next by potash-glass, and least of all by soda-glass.

The following substances yield the ingredients necessary for the formation of glass.

*Silica:* Ground quartz or flint, or quartz-sand, which is sometimes treated with hydrochloric acid to free it from adhering sesquioxide of iron. —*Potash:* Crude potash and wood-ashes (this likewise yields lime and sesquioxide of iron).—*Soda:* Carbonate of soda; sulphate of soda with charcoal (which decomposes the sulphuric acid); native and artificially prepared soda (which at the same time yields lime); common salt, by which the potash-glass—produced by using carbonate of potash—is converted into soda-glass and chloride of potassium.—*Baryta:* Heavy spar mixed

with charcoal, or carbonate of baryta; rarely employed. According to Baudrimont and Pelouze, one atom of heavy spar, with 3 atoms of sulphate of soda and 4 atoms of charcoal, yields a peculiarly brilliant, fusible, and easily worked glass, resembling *Crystal*.—70 parts (1 atom) of carbonate of potash, 54 parts (1 atom) of carbonate of soda, 99 parts (1 atom) of carbonate of baryta, and 224 parts (7 atoms) of silica yields a very transparent glass which scratches window glass. (Döbereiner, *Pogg.* 15, 243.)—*Strontia:* Sulphate of strontia with charcoal, or carbonate of strontia. 70 parts (1 atom) of carbonate of potash, 54 parts (1 atom) of carbonate of soda, 74 parts (1 atom) of carbonate of strontia, and 224 parts (7 atoms) of silica, yield a remarkably beautiful glass, specifically heavier, more refractive, and much more fusible than crown glass. (Döbereiner.)—*Lime:* Lime, after being burned and slaked to powder; chalk marl (which also yields alumina); wood ashes; the same exhausted with water; crude soda.—*Oxide of lead:* Litharge; minium, white lead, or 1 atom of galena with 3 atoms of sulphate of soda, whereby 4 atoms of sulphurous acid are evolved.—*Alumina:* Quartz-sand containing clay, marl, felspar, basalt, magnesian limestone, pumice-stone, and other minerals containing silicate of alumina and an alkali: they must not however be added in too large quantity, because the presence of too much alumina produces in the glass a tendency to crystallize. The mass of fused glass also dissolves alumina from the pots.

*Oxidizing agents*—such as nitre, arsenious acid, and peroxide of manganese—are added in the preparation of white glass, partly to oxidize the carbon contained in the wood-ashes or soda—which would render the glass brown; partly to convert the protoxide of iron into sesquioxide, inasmuch as a quantity of iron which, in the state of protoxide, would give the glass a dark bottle-green colour, will, if converted into sesquioxide, impart to it a light yellow tint of much less intensity. If too much sesquioxide of manganese is added, so that the carbon and the protoxide of iron cannot reduce it all to the state of protoxide, which dissolves in the glass without producing any colour, a portion is taken up in the state of sesquioxide, and stains the glass red; an excess of arsenious acid imparts a white turbidity to the glass.

*Substances causing turbidity.* Bone-ash produces a milkiness in the glass: *Bone-glass.* Binoxide of tin renders lead-glass opaque: *Enamel.*

*Colouring agents.* Blood-red: dinoxide of copper. Carmine-red: purple of Cassius. Violet-red: peroxide of manganese. Blue: oxide of cobalt, protoxide of copper. Green: the same substances, together with sesquioxide of iron; sesquioxide of chromium. Yellow: oxide of antimony, sesquioxide of iron. Yellow with a greenish lustre: sesquioxide of uranium.—Aventurine glass contains, according to Wöhler (*Pogg.* 58, 286), fine octohedral segments of metallic copper. (Vid. *Aventurin glass*, p. 381.)

The above ingredients, pulverized and mixed in the proper proportions, constitute the *Glass-fret.* This is, in most cases, first exposed in the *Fret-oven* to a gentle heat, which expels water and part of the carbonic acid, and diminishes the subsequent swelling or frothing up of the mass. It is then put into large crucibles called glass-pots, made of very refractory clay, six of which are commonly arranged on ledges in a circular or oblong furnace, and exposed to a continually increasing heat for twelve or more hours, till the mass becomes free from bubbles, quartz-granules, and streaks (arising from portions of glass-gall still remaining in it). Chloride of potassium, chloride of sodium, sulphate of potash

and sulphate of soda float on the surface in the form of a thin fluid stratum, which is skimmed off: the scum is called *Glass-gall*, or *Sandivir*. The glass is then formed into the required shapes and afterwards cooled from a red heat, as slowly as possible, in the *Annealing furnace*.

*Bottle-glass.*—Specific gravity about 2·732; very infusible, on account of the small proportion of potash and soda and the large quantity of alumina which it contains.—*a.* From *Souvigny:* Prepared from quartz-sand, marl, elutriated wood-ashes, and a small quantity of common salt. The phosphoric acid present in the glass arises from the phosphate of lime in the wood-ashes. (Berthier.) Its composition is nearly $3(CaO, 2SiO^2) + Al^2O^3, SiO^2$.—*b.* From St. Etienne: In the preparation of this glass, heavy spar is employed. (Berthier.)—*c.* From Epinac: Prepared by simply fusing together two different kinds of sand, one of which contains 61·7 per cent. of carbonate of lime, 35·6 of carbonate of baryta, and 1·2 of clay; the other (a mixture of quartz-sand, and felspar), 6 per cent. of potash, 2 of sesquioxide of iron, 0·7 of sesquioxide of manganese, 11 of alumina, and 80 of silica. (Berthier.)—*d.* From Sèvres: This glass is with difficulty reduced to a white mass, neither crystalline nor fibrous in its texture. (Dumas.)—*e.* Of unknown origin: Easily converted into fibro-crystalline Reaumur's porcelain. (Dumas.)

*Pale-green Glass used for medical bottles and chemical apparatus.*—Hard; bears changes of temperature better than white glass. *a*, *b*, *c*, *d*, are four French varieties analyzed by Berthier.

| | *Bottle-glass.* | | | | | *Glass for medical bottles.* | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *a.* | *b.* | *c.* | *d.* | *e.* | *a.* | *b.* | *c.* | *d.* |
| KO ..... } | 3·1 | 3·2 | 3·2 | 5·48 | 6·1 | 10·6 | 10·5 | 8·0 | |
| NaO .... } | | | | | | | | 3·0 | 16·4 |
| BaO .... | | 0·9 | | | | | | | |
| CaO .... | 22·3 | 20·7 | 18·0 | 29·22 | 28·1 | 10·0 | 16·2 | 13·0 | 15·6 |
| MgO .... | | 0·6 | 7·0 | | | | | 0·6 | 2·2 |
| MnO .... | 1·2 | | 0·4 | | | 0·3 | 1·2 | | |
| $Fe^2O^3$ .... | 4·0 | 3·8 | 4·4 | 5·74 | 6·2 | 1·5 | 2·5 | 1·6 | 0·7 |
| $Al^2O^3$ .... | 8·0 | 10·4 | 6·8 | 6·01 | 14·0 | 3·0 | 4·5 | 3·6 | 2·4 |
| $SiO^2$ .... | 60·0 | 60·4 | 59·6 | 53·55 | 45·6 | 71·6 | 62·5 | 69·6 | 62·0 |
| $PO^5$ .... | 0·4 | | | | | | | | |
| | 99·0 | 100·0 | 99·4 | 100·00 | 100·0 | 97·0 | 97·4 | 99·4 | 99·3 |

*Window-glass.*—Approximately, $NaO, 2SiO^2 + CaO, 2SiO^2$. *a* to *f* French; *g* English. *f* and *g*, the hardest and most infusible; *b*, the next; *d*, the softest and most easily fused of the whole. In France, a mixture is used of 100 parts of quartz-sand with between 30 and 40 parts of dry carbonate of soda (or as much sulphate with charcoal) and 30 to 40 parts of carbonate of lime. (Dumas.)

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* |
|---|---|---|---|---|---|---|---|
| NaO ..... | 15·22 | 11·30 | 12·88 | 17·70 | 13·7 | 10·1 | 11·1 |
| CaO ..... | 13·31 | 17·25 | 16·17 | 9·65 | 7·8 | 14·3 | 12·5 |
| $Al^2O^3$ ..... | 1·82 | 2·20 | 2·40 | 4·00 | 10·0 | 7·6 | 7·4 |
| $SiO^2$ ..... | 69·65 | 69·25 | 68·55 | 68·65 | 68·5 | 68·0 | 69·0 |
| | 100·00 | 100·00 | 100·00 | 100·00 | 100·0 | 100·0 | 100·0 |

*German Window-glass* generally consists of a double silicate of lime and potash, *e.g.* 100 parts of quartz-sand, 50 parts of pearl-ash, from 25 to 30 parts of chalk, and 2 parts of nitre. In many mixtures, however, common salt is an ingredient; or it is really a *Glauber's salt* glass, which according

to Gehlen is prepared with 100 parts of quartz-sand, 50 parts of dry Glauber's salt, 17·5 to 20 parts of lime, and 4 parts of charcoal.

*French Mirror-glass.*—Specific gravity, 2·488 ... 2·506. Containing about $2(NaO, 3SiO^2) + CaO, 3SiO^2$. The variety *a* examined by Berthier, *b* by Tassaert, *c* and *d* by Dumas. All the varieties have a bluish tinge arising from the soda (*d* the least); potash-glass is free from this defect.

*Venetian Mirror-glass.*—Containing about $KO, 3SiO^2 + 2(NaO, 3SiO^2) + 3CaO, 2SiO^2$; *e* obtained from an old mirror having a yellow tinge. (Berthier.)

*Bohemian Glass.*—Specific gravity 2·396; containing about $2(KO, 3SiO^2) + 3(CaO, 3SiO^2)$;—*f* obtained from a goblet from Neufeld in Bohemia, transparent and colourless (Berthier);—*g* from Neufeld (Gros); *h* from an old cup of Bohemian glass, perfectly transparent (Dumas); *i* ordinary Bohemian glass (Peligot.)

| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* | *g.* | *h.* | *i.* | *k.* |
|---|---|---|---|---|---|---|---|---|---|---|
| KO ..... | | | | 5·50 | 6·9 | 12·7 | 11·0 | 11·8 | 15 | 21·0 |
| NaO..... | 17·0 | 17·0 | 17·5 | 12·05 | 8·1 | 2·5 | | | | |
| CaO..... | 6·4 | 6·0 | 3·8 | 5·60 | 11·0 | 10·3 | 10·0 | 9·2 | 8 | 9·9 |
| MgO ..... | | | | | 2·1 | | 2·3 | | | |
| MnO .....<br>$Fe^2O^3$ ..... | 1·1 | 1·0 | | | 0·1<br>0·2 | 0·2<br>0·3 | 0·2<br>3·9 | | | |
| $Al^2O^3$ ..... | 2·6 | 76·0 | 2·8 | 3·50 | 1·2 | 0·4 | 2·2 | 9·6 | 1 | 1·4 |
| $SiO^2$..... | 72·0 | | 75·9 | 73·85 | 68·6 | 71·7 | 71·6 | 69·4 | 76 | 67·7 |
| | 99·1 | 100·0 | 100·0 | 100·50 | 98·2 | 98·1 | 101·2 | 100·0 | 100 | 100·0 |

*k. English Crown-glass*, of specific gravity 2·487, has a composition similar to that of Bohemian glass.

*Crystal-glass.*—Specific gravity 2·9 to 3·255. From tersilicate to tetrasilicate of oxide of lead and potash. Pure silicate of lead is yellow; but when it is combined with a sufficient quantity of silicate of potash, the mixture is colourless.—Crystal-glass is obtained from 100 parts of pure quartz-sand, 60 to 70 parts of minium or litharge, and 30 to 40 parts of purified pearl-ash; sometimes an addition is made of 4 parts of borax, 3 parts of nitre, 0·15 parts of arsenious acid, and 0·2 parts of peroxide of manganese.

*a. London Crystal-glass.*—Transparent and colourless; used in the construction of philosophical instruments; contains about $2(KO, 4SiO^2) + 3(PbO, 4SiO^2)$; examined by Berthier.

*b.* From Vonêche in Belgium; $KO, 4SiO^2 + 2(PbO, 4SiO^2)$ nearly. (Berthier.)

*c.* From Newcastle; $2(KO, 3SiO^2) + 3PbO, 3SiO^2)$, nearly. (Berthier.)

*d.* Origin unknown; $2(KO, 3SiO^2) + CaO, 3SiO^2 + 3PbO, 3SiO^2$ nearly. analyzed by Dumas.

*e.* From England; $KO, 3SiO^2 + PbO, 3SiO^2$ nearly; analyzed by Faraday.

*Flint-glass.*—Bisilicate of lead and potash, prepared from the purest materials that can be obtained: for example, 100 parts of quartz, 50 parts of carbonate of potash, 100 parts of minium, 3 parts of borax, for 0·15 parts of arsenious acid, and 0·2 of peroxide of manganese. Guinand's granut-glass has a specific gravity of 3·3 to 3·6; Frauenhofer's, a specific gravity of 3·77.—*a.* Flint glass examined by Faraday. *b.* Guinand's

flint-glass, analyzed by Dumas, $= 2(KO, 2SiO^2) + 3(PbO, 2SiO^2)$.—Döbereiner (*Schw.* 54, 424) recommends the proportions of 1 atom of potash to 2 atoms of oxide of lead and 7 atoms of silica. Faraday's flint-glass (*Pogg.* 18, 515), specific gravity = 5·44, has a very different composition, being a compound of oxide of lead with silicic acid and boracic acid.

The *Mentz Flux* or *Pierre de Strass* used in the formation of artificial gems, consists of flint-glass with a smaller proportion of silicate of potash, prepared likewise with the purest ingredients: *e g.* 100 parts of quartz or rock-crystal, 32 to 52 parts of hydrate of potash purified by alcohol (III. 13), 154 to 157 parts of minium, or 171 parts of pure white lead, 6 to 9 parts of borax, $\frac{1}{4}$ to $\frac{1}{3}$ p. c. of arsenious acid. Dumas analyzed the *Strass* manufactured by Donault-Weiland, the composition of which is nearly, $KO, 2SiO^2 + 3(PbO, 2SiO^2)$.)

| | *Crystal-glass.* | | | | | *Flint-glass.* | | Strass. |
|---|---|---|---|---|---|---|---|---|
| | *a.* | *b.* | *c.* | *d.* | *e.* | *a.* | *b.* | |
| KO..... | 9·0 | 6·6 | 9·4 | 8·9 | 13·67 | 11·75 | 11·7 | 7·9 |
| CaO .... | | | | 2·6 | | | 0·5 | |
| PbO .... | 28·2 | 34·4 | 37·4 | 32·5 | 33·28 | 43·05 | 43·5 | 53·0 |
| MnO .... | 1·0 | | | Trace. | | | | |
| $Fe^2O^3$.... | 0·4 | | 0·8 | | | | | |
| $Al^2O^3$.... | | 1·0 | 1·2 | | | | 1·8 | 1·0 |
| $SiO^2$ .... | 59·2 | 56·0 | 51·4 | 56·0 | 51·93 | 44·30 | 42·5 | 38·1 |
| | 97·8 | 98·0 | 100·2 | 100·0 | 98·88 | 99·10 | 100·0 | 100·0 |

The flint glass *b* contains also a trace of arsenious acid, and the *Strass* a trace of borax in addition.

¶ *Aventurine Glass.*—A brownish coloured glass, interspersed with small spangles, which give it a peculiar shining appearance. This glass was formerly employed in the arts and for ornaments, and its manufacture was kept secret. Gahn has observed that the spangles consist of metallic copper crystallized in the form of flat segments of a regular octohedron. (*Ann. Pharm.* 45, 134, 1843.) Fremy and Clemandot have succeeded in preparing this glass by fusing together, for 12 hours, a mixture of 300 parts of pounded glass, 40 parts of copper scales and 80 parts of iron scales, and afterwards cooling the mixture slowly. The glass thus obtained was somewhat dull, but contained copper diffused through it in octohedral crystals. (*Compt. rend.* 22, 339.)

*Ruby-glass, containing Gold.*—Splittgerber (*Pogg.* 61, 144) gives the following proportions, as affording an excellent glass of this kind: 3 lbs. 4½ oz. of fine white quartz, 1 lb. 14 oz. of nitre, 26 oz. of pure white soda (hydrate?), 8 oz. of carbonate of lime, 4½ oz. of arsenious acid, 9 oz. of minium, 8 oz. of oxide of antimony, and the solution of a German ducat, weighing 3·41 grammes, in aqua-regia. The gold solution is first poured into the sand; the remaining ingredients then added, and the whole put into a glass-pot and exposed for more than 3 hours to a white heat. This method differs from former ones, in not having any purple of Cassius or oxide of tin added, those materials having hitherto been always considered necessary. The glass thus obtained is perfectly colourless, but on being heated to a temperature of 500°, assumes an intense ruby colour. The colour, when once produced, cannot be again destroyed by exposure to heat, even in an atmosphere of oxygen or hydrogen, or in a close crucible surrounded with sand, powdered charcoal, or oxide of zinc, or by throwing the glass into a flux of nitre or chlorate of potash;

before the oxyhydrogen blow-pipe, however, it loses its colour, but regains its original tint on cooling and subsequent exposure to heat. Splittgerber accounts for the peculiarities of this glass, by assuming that the gold in the colourless variety is in the form of oxide; and that when heated a second time, it is converted into the ruby-coloured oxide described by Berzelius, in consequence of a portion of its oxygen combining with one or more of the other substances present—probably with the antimonious acid. The slight increase in bulk consequent on the second heating, appears to be in favour of this view. Splittgerber likewise succeeded in obtaining a coloured glass with purple of Cassius, but of a violet rather than a ruby tint. Rose (*Pogg.* 72, 556) gives the following proportions for ruby-coloured glass: 46 lbs. of fine quartz, 12 lbs. of borax, 12 lbs. of nitre, one lb. of minium, 1 lb. of white arsenious acid, and a solution of 8 ducats in aqua-regia. The whole is then mixed and fused as before. The resulting glass is colourless, but when again heated to redness acquires a ruby colour; Rose has likewise observed that the red colour is produced, whether the glass is heated in atmospheric air, oxygen, or carbonic acid gas. By exposure to a heat at which it softens, it becomes opaque and liver-coloured. When it is fused before the oxyhydrogen blowpipe, colourless drops are obtained, which Rose could not again obtain of a red colour by heating. Rose is of opinion that the colourless glass contains silicate of gold, and that this compound, when heated, is decomposed, with separation of oxide of gold, which imparts the red colour to the glass; moreover, that the liver-coloured glass probably contains metallic gold.

| | *Aventurin glass.* | | | | *Ruby glass.* | | |
|---|---|---|---|---|---|---|---|
| | *a.* | | *b.* | | *c.* | | *d.* |
| KO | 2·1 | | 5·5 | | 23·41 | | 6·70 |
| NaO | 8·2 | | 7·1 | | | | 5·79 |
| CaO | 8·0 | | 8·9 | | 2·01 | | 3·80 |
| MgO | 4·5 | | | | | | 0·50 |
| $Fe^2O^3$ | 6·5 | FeO | 3·5 | | | | 2·20 |
| $Al^2O^3$ | | | Traces. | | | | |
| $SiO^2$ | 65·2 | | 67·7 | | 64·17 | | 58·98 |
| $PO^5$ | 1·5 | | | | | | |
| Cu | 3·0 | | 3·9 | | | | |
| Sn | Traces. | $SnO^2$ | 2·3 | | | $SnO^2$ | 0·69 |
| Sb | | | | | 2·40 | | |
| As | | | | | | | Traces. |
| Pb | | | 1·1 | | 5·06 | | 22·93 |
| An | | | | | 0·06 | | 0·40 |
| | 99·0 | | 100·0 | | 97·11 | | 101·99 |

*a.* Aventurine from Venice, analysed by Gahn.—*b.* Analysed by Peligot.—*c.* Ruby-glass, analysed by Splittgerber, the gold found by experiment amounting to less than one-half the quantity per cent. added. —*d.* Venetian ruby-glass, in the form of round flattened masses, distinguished from the ordinary varieties by being very fusible, and not losing its red colour when melted; analysed by Böhme. (*Erdm. & March. J.* 38, 335.) ¶

*Enamel* is, for the most part, a double silicate of lead and potash, rendered opaque by binoxide of tin. In one specimen of enamel, Dumas found 8·3 per cent. of potash, 50·3 of oxide of lead, 9·8 of binoxide of tin, and 31·6 of silica. Antimonious or arsenious acid produces a similar

effect to the binoxide of tin. By adding colouring agents, principally metallic oxides (III., 378) to white enamel, the coloured varieties are obtained. [See Wächter (*Ann. Pharm.* 69, 99) on porcelain colours for enamel, &c.]

[On the subject of glass, see more particularly: Dumas, *Ann. Chim. Phys.* 44, 144; also *J. Pharm.* 16, 675; further in his *Handb. d. angew. Chemie.* 2, 579;—Berthier, *Ann. Chim. Phys.* 44, 433.]

*Decomposition of Glass.*—1. Water extracts potash or soda from glass, together with a portion of silica, the decomposition taking place with greater ease in proportion as the glass is richer in these alkalis and more minutely divided, and the temperature of the water higher. The powder filed off from a tube of white glass reddens moistened turmeric-paper. (Bischof, *Kastn. Arch.* 1, 443.) Finely-pounded plate-glass acts in a similar manner. (Faraday, *Pogg.* 18, 569.) Water triturated with pounded glass in an agate mortar becomes alkaline, and on the addition of sal-ammoniac deposits flakes of silica. (Fuchs, *Kastn. Arch.* 5, 396.) Water becomes alkaline after long digestion with glass at a boiling heat, and likewise turbid from separation of an insoluble compound of silicic acid and lime. (Dumas.) An alkaline reaction is exhibited by the powder of bottle-glass, and of Reaumur's porcelain formed from it; of plate-glass, crown-glass, flint-glass, and white enamel. After sufficient washing, it no longer reddens turmeric-paper, unless it be recrushed in a mortar. 100 parts of finely-divided flint-glass boiled for a week with water, lose 7 parts of potash, which may be obtained in the solid state by evaporation. (Griffiths, *Quart. J. of Sc.* 20, 258.) The moisture in the atmosphere produces a similar alteration, separating the potash and soda, and leaving the greater part of the silica with the lime on the surface of the glass: glass thus decomposed often exhibits prismatic colours on its surface. Sometimes this superficial decomposition is scarcely visible; but, on warming the glass, numerous fine scales peel off, and leave the surface dull, opaque, and wrinkled. This fault shows itself in glass to which, for the sake of economizing fuel, too small a quantity of silica has been added. The pearly stratum with which specimens of antique glass found buried in the earth are covered, consists almost wholly of silica. (Griffiths.) Glass which has lain in a pit at least ten feet deep in the ground, is soft when dug up, and may be bent and indented, and even cut in two with a knife [hydrate?]; but after exposure to the air for a few hours, it again hardens,—and if it has been previously bent or twisted, it becomes very brittle, like unannealed glass. (Colladon, *J. Chim. Med.* 16, 579.)

2. All kinds of glass are corroded by hydrofluoric acid, with formation, partly of fluoride of silicium, partly of the double fluorides of silicium and potassium, sodium, calcium, &c. A hot concentrated solution of phosphoric acid likewise decomposes every variety. Glass which is poor in silica is attacked by boiling oil of vitriol; and glass of yet inferior quality—that, namely, which becomes dull on exposure to heat (Dumas)—is acted on by boiling hydrochloric and nitric acids and aqua-regia (a dull spot remaining after evaporation of the acid). (Berzelius.) The acids dissolve out potash, soda, lime, and other bases, and separate the silica. On pounded glass they act with much greater energy. From pulverized flint-glass, boiling hydrochloric acid extracts potash only, not the oxide of lead. (Griffiths.) Many kinds of bottle-glass which resist the action of acetic acid are decomposed by the stronger mineral acids; thus

a bottle filled with sulphuric acid will sometimes, at ordinary temperatures, gradually become covered with warty depressions, which at last penetrate through the substance of the glass. (Dumas.) In distilling hydrochloric acid from a green glass retort, Hess (*Pogg.* 20, 540) obtained a crystalline sublimate [?] of silica, while chloride of potassium, sesquioxide of iron, and silica were dissolved. Many anhydrous salts of ammonia containing the stronger acids, also attack glass—especially lead-glass—when heated in contact with it; such is the case with a mixture of hydrochlorate and nitrate of ammonia (Silliman), or with sulphate or bisulphate of ammonia (Marchand, *Pogg.* 42, 556.)

3. Solutions of potash and soda dissolve out the silica of glass with greater ease in proportion to their temperature and degree of concentration. Even at ordinary temperatures, the alkaline liquid partially dissolves the glass bottle in which it is preserved, frequently causing it to crack (III., 14). Even ammonia attacks many kinds of glass; a bottle made of flint-glass, and containing a solution of carbonate of ammonia, became so fragile, that, on shaking it, pieces of glass were detached. (Griffiths.)

4. Glass containing oxide of lead blackens when heated in the flame of a lamp or in hydrogen gas, from reduction of the oxide of lead—and when heated in sulphuretted hydrogen, from formation of sulphide of lead. From this cause, Guinand's flint-glass becomes tarnished in dwelling-houses. (Faraday.) A bottle made of French glass, in which hydrosulphate of ammonia had been kept, acquired a metallic lustre, from formation of sulphide of lead. (Bischof, *Br. Arch.* 17, 242.)

*Crystallized or Devitrified Glass.—a.* Many kinds of glass, when slowly cooled in the pots, separate into two portions, the one crystallizing in opaque prisms and needles, the other retaining its vitreous character. According to the following analysis of Dumas, it appears that the portion which crystallizes gives up soda to that which remains in the vitreous state.

| | Crystallized portion. | | Vitreous portion. |
|---|---|---|---|
| NaO ..... | 14·9 | ..... | 19·8 |
| CaO ..... | 12·0 | ..... | 12·0 |
| $Al^2O^3$ ..... | 4·9 | ..... | 3·5 |
| $SiO^2$ ..... | 68·2 | ..... | 64·7 |
| | 100·0 | ..... | 100·0 |

*b. Reaumur's Porcelain.*—Many kinds of glass, after exposure for several hours to a heat at which they become soft,—in a potter's furnace, for example—pass into a condition resembling porcelain. Bottle glass is the most disposed to undergo this change, doubtless from the greater quantity of alumina which it contains; next in order is the more common sort of green window glass; white glass rich in lime is also liable to this change, but not pure silicate of potash or soda, or lead-glass. (Lewis, Dartigues.)

The devitrification takes place equally well if the glass vessels are surrounded within and without with an infusible powder or *cement*, to prevent them from losing their shape—*e. g.*, sand, a mixture of sand and gypsum, bone-ash, clay, powdered bricks, lime, sesquioxide of iron, charcoal, or soot—as when they are heated by themselves; but in the former case, a longer time is required. (Lewis, Dartigues, Morveau.)—It occurs also in a similar manner with glass enveloped in a lava-stream. (Morveau.) This change may either be regarded, according to Dartigues' supposition,

as arising simply from the amorphous glass passing without change of composition into the crystalline state—the long continued state of softness affording the atoms an opportunity of uniting together in crystalline molecules; or we may suppose with Lewis, Morveau, and Dumas, that the glass in undergoing this change loses a portion of its alkali, which, when the glass is ignited by itself, passes off in vapour, and when it is surrounded by a powder during ignition, is absorbed by the powder. Dumas is moreover of opinion that the protoxides of manganese and iron present in the glass are peroxidized at the same time. According to Lewis, the sand which surrounds the glass as *cement*, becomes caked together by absorbing alkali. Dumas found in a devitrified specimen of bottle glass, only 2 per cent. of potash, together with 27·4 per cent. of lime, 6·6 of the sesquioxides of manganese and iron, 12·0 of alumina, and 52·0 of silica [the behaviour of Reaumur's porcelain in fusing is also in favour of this theory. *Vid. seq.*].

In this change, the following stages are to be distinguished: 1. The glass becomes cloudy, and appears blue by reflected and yellow by transmitted light (Lewis, Fournet), still however exhibiting a vitreous fracture. The blue colour is also seen at the fractured edges, and consequently cannot proceed from oxidation. (Fournet.) The opacity doubtless arises from the separation of fine particles whose composition differs from that of the rest of the mass. Many iron-slags behave in a similar manner (especially the double silicate of alumina and lime). Many slags which appear green when cooled rapidly, become blue within and yellow by transmitted light, when slowly cooled, even if they are green on the outside; but the powder again assumes a green colour. This fact would appear to explain the action of the test which is employed to distinguish many earths and heavy metallic oxides by the blowpipe: viz., that the bead obtained by fusing them with borax or microcosmic salt, remains clear when rapidly cooled, but becomes turbid and opaque by exposure to *interrupted blasts*, or *flaming*, whereby it is kept for a long time in a soft state, and crystalline compounds are produced and separated. (Fournet, *Ann. Chim. Phys.* 79, 370; also *J. pr. Chem.* 26, 321.)

2. After this stage, white, opaque needles are formed, proceeding from the inner and outer surfaces of the glass, and finally meeting in the centre. The surface of contact is often marked by a brown line. The mass thus far changed is *Reaumur's porcelain*. When burnt between pipe-clay it has a smooth surface, but if burnt between lime or bone-ash, it acquires a rough, wrinkled, or blistered surface. When burnt between powdered charcoal, its surface becomes black or grey. (Lewis.) It is white and nearly opaque, exhibiting a straight, fibrous texture at the fractured surface; it is specifically heavier than glass, and so hard that it scratches glass and sometimes even rock crystal, and emits sparks with steel; it does not crack so readily by change of temperature as glass, or even as porcelain, and conducts heat and electricity better than the former, so that, unless insulated, it does not become electrical by friction. Reaumur's porcelain may be used instead of ordinary porcelain in the fabrication of utensils. It fuses with much greater difficulty than glass, and is thereby converted into a white or grey enamel, transparent only at the edges—having a conchoidal fracture—harder than glass, but softer than Reaumur's porcelain. The specific gravity of this enamel is to that of the substance before fusion as 2·625 : 2·801. It does not become electrical by friction. (Morveau.)

3. If the baking be too long continued, the threads of the fibrous

structure become separated by fissures, and the whole is converted into a fine-grained and subsequently into a coarse-grained mass, loose, greyish, and still more difficult of fusion. When the porcelain has begun to change from the fibrous to the granular condition, it may still be fused by the heat of a forge into a pearly, porous mass, which contains green glass enclosed within. If the change to the fine-grained condition is complete, it fuses to a spongy mass; but when the coarse-grained state is arrived at, it no longer fuses, but cakes together into a very hard mass, having a dense fracture. (Lewis, *Physico-chemical Memoirs; translated into German* by Krünitz, 1, 425; compare also Dartigues, *Ann. Chim.* 50, 325; also *Schw.* 2, 112; Guyton Morveau, *Ann. Chim.* 83, 113; also *Schw.* 2, 137.)

B. Carbonate of Silica and Soda.—A boiling aqueous solution of carbonate of soda dissolves moderately ignited silica or its hydrate in large quantity, and deposits it again in a gelatinous form on cooling. (Pfaff, *Schw.* 29, 383.) If alumina is mixed with the silica, it remains undissolved, in combination with a large portion of the silica and with soda. (Forchhammer, *Pogg.* 35, 335.)

C. Silica dissolves in fused borax slowly but completely, forming a clear and difficultly fusible glass.

D. Microcosmic salt dissolves silica but very slowly when fused with it before the blowpipe; the bead remains clear on cooling. The portion of silica which remains undissolved has the form of a transparent, swollen mass. (Berzelius.)

E. Fluoride of Silicium and Sodium.—Formed like the potassium compound, by mixing hydrofluosilicic acid with an aqueous solution of soda or of a soda-salt (Scheele, Berzelius); it separates with greater facility than the above, without however producing rainbow tints. The gelatinous precipitate collected on a filter, crumbles, on drying, to a white powder; and its aqueous solution yields on evaporation, small, shining, probably regular six-sided prisms, perpendicularly truncated. (Berzelius.)

| | Crystallized. | | Or: | | | Berzelius. |
|---|---|---|---|---|---|---|
| Na | 23·2 | 24·60 | $NaO$ | 31·2 | 33·09 | 32·844 |
| Si | 15·0 | 15·91 | $SiO^2$ | 31·0 | 32·87 | 31·600 |
| 3F | 56·1 | 59·49 | $3(F-O)$ | 32·1 | 34·04 | 33·215 |
| $NaF, SiF^2$ | 94·3 | 100·00 | | 94·3 | 100·00 | 97·659 |

It fuses before ignition, and behaves in the fire like the double fluoride of silicium and potassium; but it gives up the first portions of fluoride of silicium with greater facility, and then solidifies; the remainder of the fluoride of silicium is evolved only at a high temperature. If fragments of carbonate of ammonia are projected into the ignited crucible, the fluoride of silicium is more readily evolved, but a portion of silica is afterwards found in the residue. Heated with potassium, it is resolved into fluoride of sodium, fluoride of potassium, and pure silicium. It is decomposed by digestion with an aqueous solution of boracic acid; but the silica is far from being completely separated. When it is boiled with an aqueous solution of carbonate of soda, decomposition takes place, carbonic acid gas is evolved, and the liquid assumes a gelatinous consistence. It is

much more soluble than the potassium compound, especially in hot water. Excess of acid does not increase its solubility. (Berzelius.)

F. Fluoride of Sodium containing Silica.—Fluoride of sodium fuses with silica at a temperature at which it is not fusible when alone. The mass does not evolve gaseous fluoride of silicium at a strong red heat. (Berzelius.)

G. Soluble Glass containing Potash and Soda.—A mixture of one atom of carbonate of potash and one atom of carbonate of soda fuses with six atoms of silica, at a gentle red heat, forming a transparent glass, which, when reduced to powder, dissolves in boiling water, forming a solution thinner than that of the potash soluble glass. (Döbereiner, *Pogg.* 15, 243.)

## Silicium and Lithium.

Fluoride of Silicium and Lithium.—$LF, SiF^2$. Crystallizes from a solution in hydrofluosilicic acid, in small transparent grains, which, under the microscope present the appearance of six-sided prisms. The salt has a slightly acid and bitter taste; it fuses at a red heat, and obstinately retains its fluoride of silicium. Pure water dissolves it very slowly; acidulated water more readily. (Berzelius.)

## Silicium and Barium.

A. Silicate of Baryta.—One part of silica heated to whiteness with $\frac{1}{4}$ of its weight of baryta, yields a white brittle mass,—with $\frac{1}{3}$ baryta, a hard, brittle mass, translucent at the edges,—with $\frac{1}{2}$ baryta, a fused, porous mass resembling porcelain,—with one part of baryta, a hard unfused mass,—with 2 or 3 parts of baryta, a vitrefied, porous mass like porcelain in appearance,—with 4 parts of baryta, a nearly opaque mass, fused at the edges only. With 2 parts or more of baryta, the compound is soluble in acids. (Kirwan.)—According to Vauquelin, 1 part of silica with 3 parts of baryta, produces a pale green, solid mass, which is soluble in acids.

B. Fluoride of Silicium and Barium.—A mixture of the aqueous solutions of terhydrofluate of silica and hydrochlorate of baryta, appears clear at first, but after a short time deposits a great number of small, hard crystals. (Gay-Lussac & Thénard.)—Nearly all the baryta is precipitated, a trace only remaining dissolved in the hydrochloric acid. If the solutions are mixed at a boiling heat, the crystals obtained on cooling are somewhat larger, but still only microscopic; they consist of prisms with acute summits. (Berzelius.)—The compound is easily resolved by ignition into gaseous fluoride of silicium and fluoride of barium, which remains behind. Ignited with oil of vitriol, it leaves 82·933 per cent. of sulphate of baryta. It is but very sparingly soluble in water, but dissolves rather more freely in hot water than in cold; the presence of hydrochloric acid, however, does not increase its solubility. (Berzelius.) ¶ Fresenius states that its solubility in pure water at ordinary temperatures is 1 part in 3,802 parts; but in water acidulated with hydrochloric acid, 1 part in 733 parts. (*Ann. Pharm.* 59, 117, 1846.) ¶

| | Calculation. | | Berzelius. |
|---|---|---|---|
| BaF | 87·3 | 62·49 | 62·255 |
| $SiF^3$ | 52·4 | 37·51 | 37·745 |
| BaF, $SiF^3$ | 139·7 | 100·00 | 100·000 |

C. Silicate of Baryta and Potash.—This salt, which, according to Dalton, contains equal numbers of atoms of baryta and potash, is precipitated on mixing solution of silica with baryta-water.

## Silicium and Strontium.

A. Silicate of Strontia.—One part of silica fuses with an equal weight of strontia, partly to an amber-coloured glass, partly to a black and white enamel. (Kirwan.)—With 3 parts of strontia, it forms a solid, grey, sonorous mass, which is nearly tasteless, and dissolves but sparingly in water, though readily in aqueous acids. (Vauquelin.)—Carbonate of strontia, digested in solution of silica, is converted into dense hydrated silicate of strontia. (Kuhlmann.)

B. Fluoride of Silicium and Strontium.—A solution of carbonate of strontia in hydro-fluosilicic acid, yields after evaporation and cooling, short, hydrated, rhombic prisms, with dihedral summits resting on the two acute lateral edges. The crystals are converted by heat into the opaque anhydrous compound. On treating them with water, a small quantity of a basic salt remains undissolved, and the liquid contains excess of acid. In acidulated water, they dissolve readily and without suffering decomposition. (Berzelius.)

C. Silicate of Strontia and Potash.—Prepared by precipitating the silica solution with strontia-water. (Dalton.)

## Silicium and Calcium.

A. Silicate of Lime.—*a. Disilicate.*—$2CaO, SiO^2$.—Obtained by exposing one atom of pure quartz and 2 atoms of marble in a charcoal crucible to a full white heat in Sefström's blast-furnace (II., 35). The mixture does not fuse; but by employing a somewhat smaller quantity of marble, a fused mass is obtained, which, after being taken out of the crucible, crumbles to pieces in a minute, without alteration of weight, and contains 58·77 per cent. of lime to 41·10 of silica. (Sefström, *J. Techn. Chem.* 10, 145.)

*b. Monosilicate.*—Found native in the form of *Tabular spar* or *Wollastonite.*—Belongs to the oblique prismatic system of crystallization, has two cleavage-planes parallel to the faces of the rhombic prism, of 93° 18′ and 84° 42′; specific gravity = 2·8—2·9; hardness, equal to that of apatite.—White; translucent; fuses with difficulty before the blowpipe to a semi-transparent glass; decomposed perfectly by hydrochloric acid, either before or after ignition, with separation of gelatinous silica. Walchner (*Schw.* 47, 245) found at the bottom of an iron-smelting furnace a mass of *artificial tabular spar,* having a laminated fracture, greyish white and translucent, likewise decomposable by hydrochloric acid, but containing 7·8 per cent. of alumina. By fusion in a smith's

forge, a bluish grey, slightly translucent mass is obtained, resembling chalcedony, of specific gravity 2·86, and with a fracture partly splintered, partly crystalline. (Sefström.)

| | *Tabular spar.* | | H. Rose. | | Stromeyer. |
|---|---|---|---|---|---|
| CaO | 28 | .... | 47·46 | .... 47·35 | .... 47·412 |
| $SiO^2$ | 31 | .... | 52·54 | .... 52·65 | .... 51·445 |
| MnO, 0·257; | FeO, 0·401; | | HO, 0·076; | | .... 0·734 |
| CaO, $SiO^2$ | 59 | .... | 100·00 | .... 100·00 | .... 99·591 |

Hydrate of silica added to lime-water precipitates a powder resembling tabular spar. (Fuchs.)

*c. Sesquisilicate.*—$2CaO, 3SiO^2$.—Prepared by exposing 2 atoms of marble with 3 atoms of quartz to the heat of a smith's forge. Fuses much more readily than *b*; its specific gravity is 2·74. Moreover, it exactly resembles *b* in external appearance, but is somewhat more brittle. (Sefström.)

*d. Bisilicate.*—$CaO, 2SiO^2$.—*α. Anhydrous.*—One atom of marble heated in a blast-furnace, with 2 atoms of quartz, yields a difficultly fusible mass, the under portion of which is denser and richer in silica than the upper, which is porous. (Sefström.)

*β. With one atom of water.*—$CaO, 2SiO^2$, Aq.—This appears to be the composition of Shepard's *Dauburite*. (*Sill. Amer. J.* 25, 137.)

*γ. With 2 atoms of water.*—*Okenite* or *Dysklasite.*—A mineral of radiated, fibrous texture, and specific gravity = 2·28; white, with a pearly lustre; swells up before the blowpipe, and fuses to a porcelain-like mass. With borax it gives a colourless bead, but dissolves with difficulty and imperfectly in microcosmic salt. In the state of powder, it is easily decomposed by cold hydrochloric acid (but no longer after ignition) with separation of gelatinous flakes of silica. (Kobell, *Kastn. Arch.* 14, 333.)

| | *Okenite.* | | | Von Kobell. |
|---|---|---|---|---|
| CaO | 28·0 | .... | 25·92 | .... 26·59 |
| $2SiO^2$ | 62·0 | .... | 57·41 | .... 55·64 |
| 2HO | 18·0 | .... | 16·67 | .... 17·00 |
| Alumina and Sesquioxide of Iron | | .... | | .... 0·53 |
| Ca, $2SiO^2 + 2Aq$ | 108·0 | .... | 100·00 | .... 99·76 |

*e. Tersilicate.*—$CaO, 3SiO^2$.—One part of marble fuses with 3 parts of quartz, forming a homogeneous, blistered, pearl-grey mass. (Sefström.)

Chalk, gypsum, and even phosphate of lime, decompose an aqueous solution of silicate of potash or soda into alkaline carbonate, &c., and hydrated silicate of lime, which forms on the surface into a hard mass capable of being polished, but rapidly crumbles to pieces on exposure to the air. (Kuhlmann, *Ann. Pharm.* 41, 220.)

## *Hydraulic Mortar.*

A pasty mixture of lime, silica, and water, which, when immersed in water, is gradually converted into silicate of lime containing water of crystallization, and hardens to a compound resembling zeolite. This salt may likewise be mixed with silicate of alumina, double silicate of alumina and magnesia, &c., according to the nature of the materials used.

The silica must be in such a state as to be capable of combining with the lime in the wet way. This hydraulic mortar is prepared either by mixing pure lime (*rich lime, fetter kalk*) previously burned and slaked to the consistence of paste, with suitable siliceous materials—the so-called *cements*—or by burning natural or artificial mixtures of lime with siliceous substances, and working up the *poor lime* (*magerer kalk*) thus obtained with water.

1. *Pure or Fat Lime with Cement.*—From 4 to 5 parts of finely powdered cement are used with one part of lime, which is slaked either before or after being mixed with the cement. The mixture, which forms a stiff paste, is then placed under water, either immediately or after exposure to the air for a few hours, and left immersed for a period of three months. Many kinds of mortar begin to harden the first day; others not till after the lapse of several days; the latter, however, often acquire the greatest degree of solidity. A high temperature favours the action. Quartz, however finely pounded, does not combine with the prepared lime, even in the course of three months. (Fuchs.) According to Petzhold, however, (*J. pr. Chem.* 16, 96) the lime does take up a very small portion of silica from the quartz. An intimate mixture of 8 parts of powdered quartz and one part of lime, ignited till it bakes together, yields a cement, 5 parts of which with one part of lime (slaked with water) solidifies slowly, but becomes very hard. Most kinds of opal yield a tolerably good cement; also, the silica precipitated from solution of silica by sal-ammoniac. Sodalite, analcime, and stilbite, form good cements; but their power of combining with lime is destroyed by ignition. Trass, pozzolano, brick-clay burnt to incipient fusion, potter's clay burnt to various degrees of hardness, according to its nature (many kinds require to be ignited with lime), moderately ignited porcelain-clay from Passau, and most of the slags from iron-furnaces, yield a very good cement. From many kinds of clay, potash is set free by this process. Pitch-stone, obsidian, and pumice-stone yield a cement of medium hardness, but require a long time to set. Felspar, in the course of five months, forms a slightly coherent mortar; after fusion, especially with lime, it becomes more efficacious. Glass behaves like fused felspar. Unignited prehnite is ineffective; but, after strong ignition, it produces a good cement. Silicates rich in magnesia, such as steatite, talc, tremolite, and diopside, are of very little use, even after ignition; the silica in these minerals is already combined with too much magnesia, and partly also with lime, to be able to take up much more from the slaked lime. It is only by fusion in a blast-furnace, during which it emits sparks [and takes up silica and alumina from the crucible ?] that steatite can be made to yield a tolerably good mortar. Tabular spar, even when burnt, lievrite, and the slag produced in the conversion of cast-iron into wrought-iron, have no action on lime.

With these cements, burnt and slaked dolomite hardens more rapidly and firmly than burnt lime. When minerals containing potash, soda, or lithia are employed, the greater part of these alkalis are set free by the lime and imparted to the water, and in great abundance, if more lime is used than is required for the production of the mortar. This occurs with natrolite, analcime, leucite, felspar (which gives up 10 per cent. of potash), lithia-mica, pitchstone, obsidian, pumice, and a great number of clays. Burnt dolomite expels these alkalis even better than burnt lime. *(III., 358.)*

The setting of the mortar is assisted to a certain extent by the carbonic acid which the water takes up from the air: at all events, mortar which has been under water for a long time is hardest at the surface, and effervesces at that part with acids. On soft mortars, however, the carbonic acid may exert a decomposing action. Well set mortar is as hard and solid as limestone. Its specific gravity is lower in proportion to the amount of water present; and, consequently, mortar prepared with precipitated silica and slaked lime, is the lightest of all. The mortar forms a jelly with hydrochloric acid, inasmuch as the acid separates the silica combined with the lime. But the interior of the cement-powder remains unaltered, because it is enveloped and held together by the mortar produced. (Fuchs.)

2. *Natural or artificial mixture of Limestone with Siliceous Substances.* *a. Natural Mixture*, or *Hydraulic Limestone.*—This is *Marl*, which is a mixture of carbonate of lime with clay (hydrated silicate of alumina). It is best adapted for the purpose, when it contains 1 part of clay to 3 parts of carbonate of lime. If the clay is in much smaller proportion, it is necessary to add a cement after burning and slaking the lime: on the contrary, when the quantity of clay in the hydraulic lime is too great, fat slaked lime must be added. The more intimately the carbonate of lime and clay are mixed in the native mineral, the better. When hydraulic lime is ignited, the lime unites with the silica and alumina present in the clay, so that it yields gelatinous silica when treated with hydrochloric acid. The larger the proportion of clay in the mixture, the less must be the heat employed, so that the mass may not fuse. But limestone containing less than 20 per cent. of clay is almost infusible. Hydraulic lime, after being burned and reduced to powder, solidifies when made into a paste with water, because the double silicate of alumina and lime produced in the burning, absorbs water of crystallization. If the marl has been so slightly burned that it still retains carbonic acid, it frequently hardens with remarkable rapidity, because the dicarbonate of lime present enters into combination with water (III., 185). (Fuchs, *Pogg.* 27, 591.)

[For the analysis of various kinds of calcareous marl used as hydraulic lime, including those from the Island of Sheppey, which yield the so-called *Roman cement*, *vid.* H. Meyer and Kersten, *J. pr. Chem.* 24, 405: 25, 317.]

When marl is digested in dilute hydrochloric acid, the clay is left as an insoluble residue. Most kinds of marl contain more salts of potash and soda, than pure limestone. Potash and soda facilitate the union of the silica with the lime on burning, as they first combine with the silica, and then give it up to the lime. In the absence of a more soluble alkali, the combination of the lime with the silica is but imperfectly effected by ignition. A better kind of hydraulic lime is consequently obtained by intimately mixing unignited marl with 5 per cent. of potash. (Kuhlmann, *Ann. Pharm.* 41, 220. *Vid. seq.*)

*b. Artificial Mixture.*—Four measures of chalk with one measure of clay. (Berthier.) Six measures of slaked lime with one measure of clay. (Vicat.) The materials are intimately mixed, and the mixture formed into balls, burnt, and ground to powder. In England, a mixture of chalk and pulverized flint is burnt in a kiln. Hydraulic lime prepared by the latter method and reduced to powder, slakes slowly in water, becoming very tenacious, and ultimately solidifying to a white, hard, fine-grained mass, capable of receiving a polish, and containing 51·9 per cent. of lime,

3·4 of magnesia and alumina, 15·0 of combined silica, (which on treating the mass with acids, is separated in the gelatinous state,) 1·4 of unaltered sand, and 28·0 of water and carbonic acid. (Berthier.)

¶ Kuhlmann has succeeded in forming artificial limestones, by mixing a solution of silica or alumina in aqueous potash or soda with lime or chalk, or even with a solution of sulphate of alumina or common alum. If the silica solution is mixed with powdered chalk, the pasty mass gradually becomes solid in the air, and acquires a degree of hardness equal to that of the best hydraulic cements. When pieces of chalk or porous limestone are dipped into a solution of silicate of potash and exposed to the air for several days, they become hard enough to scratch limestone, and take a good polish. Burnt gypsum may be hardened in a similar manner. It is decomposed by alkaline silicates much more rapidly and completely than carbonate of lime. It may also be hardened by moistening it with a solution of alum, and afterwards burning it. Kreating (*Polytech. Centralb.* 1847, 126) produces the same effect by wetting the burnt gypsum with a solution of 1 lb. of borax in 9 lbs. of water, and subsequently igniting it strongly for six hours. The hardening is still more complete when 1 lb. of tartar and a double quantity of water is added to the solution. In the hardening of these artificial stones, the carbonic acid of the air plays the principal part, inasmuch as it decomposes the silicate of potash and separates the silica, which then contracts, and thereby contributes greatly to the hardening of the mass. If air be excluded, this effect is not produced. A solution of silicate of potash exposed to the air, solidifies in the course of a fortnight, and forms a transparent jelly, which gradually acquires great hardness without losing its transparency, and after a few months becomes hard enough to scratch glass. Kuhlmann suggests that the formation of crystallized silicic acid in limestone rocks, and likewise that of flint, agate, &c., may be due to the decomposition of silicate of potash by carbonic acid. In corroboration of this view, it is found that these minerals, after being ignited and pulverized, exhibit a distinct alkaline reaction. ¶

Hydraulic lime, both natural and artificial, is mixed (after being powdered, and before it is slaked) with fine quartz-sand, in the proportion of one part of hydraulic lime to $\frac{2}{3}$ of sand, for underground or subaqueous structures, but 1 part of lime to $2\frac{1}{2}$ parts of sand for plastering walls. (Berthier.)

[On the subject of hydraulic mortar, *vid.* Berthier, *Ann. Chim. Phys.* 22, 62; 44, 113; Vicat, *J. Phys.* 86, 189; *Ann. Chim. Phys.* 5, 387; 15, 365; 23, 69, & 424; 32, 197; 34, 102; 66, 93.

*Common Mortar which dries in the air* is a mixture of pure (fat) lime slaked to a creamy consistence, with fine and coarse quartz-sand, limestone, &c., which does not act chemically on the lime. Solidification is effected partly by drying, partly by absorption of carbonic acid from the air.

B. Borate and Silicate of Lime.—a. *With one Atom of Water.*—*Datolite.*—$CaO, BO^3 + CaO, 2SiO^2 + Aq$. Oblique rhombic prisms. *Fig.* 107 and other forms, $i : t = 91° 41'$; $u : u^1 = 77° 30'$. Specific gravity = 3·344 (Stromeyer); hardness, between felspar and apatite. Colourless, transparent or translucent.

At a full red heat, it gives off water and becomes opaque. Before the blowpipe it swells up and fuses readily to a colourless glass, imparting at the same time a green colour to the flame. In microcosmic

salt it is but partially soluble. Hydrochloric acid dissolves it and separates gelatinous silica.

b. *With 2 atoms of Water.—Botryolite.*—$CaO, BO^3 + CaO, 2SO^3 + 2Aq.$ —Kidney-shaped, and of a delicate fibrous texture.

| | *Datolite.* | | | Stromeyer. | | Rammelsberg. |
|---|---|---|---|---|---|---|
| $2CaO$ | 56·0 | 34·61 | | 35·67 | | 35·41 |
| $2SiO^2$ | 62·0 | 38·32 | | 37·36 | | 37·65 |
| $BO^3$ | 34·8 | 21·51 | | 21·26 | | 21·24 |
| $HO$ | 9·0 | 5·56 | | 5·71 | | 5·70 |
| | 161·8 | 100·00 | | 100·00 | | 100·00 |

| | *Botryolite.* | | | Rammelsberg. |
|---|---|---|---|---|
| $2CaO$ | 56·0 | 32·79 | | 34·27 |
| $2SiO^2$ | 62·0 | 36·30 | | 36·39 |
| $BO$ | 34·8 | 20·37 | | 18·34 |
| $2HO$ | 18·0 | 10·54 | | 10·22 |
| Alumina and Sesquioxide of Iron | | | | 0·78 |
| | 170·8 | 100·00 | | 100·00 |

C. Fluoride of Silicium and Calcium.—Levigated fluor-spar and finely divided silica are digested in dilute hydrofluoric acid; or carbonate of lime is added to terhydrofluate of silica as long as it is dissolved, and the solution is then evaporated at a gentle heat to the crystallizing point. Four-sided, obliquely truncated prisms. Leaves, on ignition, 36·2 per cent. of fluoride of calcium, and by ignition with sulphuric acid, 63·69 per cent. of sulphate of lime. Ignited with six times its weight of oxide of lead, it evolves 16·21 per cent. of water. When it is mixed with water, one portion is resolved into an insoluble residue of silica and fluoride of calcium, and into hydrofluosilicic acid, by which the remaining portion of the salt is dissolved without decomposition. It dissolves completely in hydrofluosilicic acid. By evaporating the solution, the above crystals are again obtained. Hydrochloric acid likewise dissolves it without decomposition; but if the solution is rapidly evaporated, hydrofluosilicic acid is evolved, and hydrochlorate of lime is produced. By adding ammonia to a recently prepared solution of the salt in hydrochloric acid, fluoride of calcium and silica are precipitated, while hydrochlorate and hydrofluate of ammonia remain dissolved. (Berzelius.)

| | Calculation. | | Or: | | | Berzelius. |
|---|---|---|---|---|---|---|
| Ca | 20·0 | 18·33 | $CaO$ | 28·0 | 25·67 | 26·40 |
| Si | 15·0 | 13·75 | $SiO^2$ | 31·0 | 28·41 | |
| 3F | 56·1 | 51·42 | $3(F-O)$ | 32·1 | 29·42 | |
| $2HO$ | 18·0 | 16·50 | $2HO$ | 18·0 | 16·50 | 16·25 |
| $CaF, SiF^2 + 2Aq.$ | 109·1 | 100·00 | | 109·1 | 100·00 | |

D. Silicate of Lime and Potash.—*a.* Many kinds of glass are thus constituted.

*b.* According to Dalton, the precipitate which lime-water produces in solution of silica, contains potash as well as silica and lime.

*c. Apophyllite* (*Ichthyophthalme, Tesselite, Oxhaverite*).—Crystalline system, the square prismatic. (*Fig.* 28, 29, 32, and others.) $p : e = 119° 30'$; $q : e = 127° 59'$; cleavage distinct parallel to $p$; less distinct parallel to $q$. Specific gravity = 2·3335. (Hauy.) Colourless, transparent, and of a pearly lustre on the cleft surfaces parallel to $p$.—

Swells up in the blowpipe flame, and fuses readily to a blistered glass. By hydrochloric acid it is first resolved into scales which reflect a variety of colours, and afterwards dissolved with separation of silica in a gummy mass. After ignition it is with difficulty acted on by hydrochloric acid; but after fusion and pulverization, decomposition takes place with somewhat greater facility.

| | *Apophyllite.* | | | Berzelius. | | Stromeyer. | | C. Gmelin. |
|---|---|---|---|---|---|---|---|---|
| KO | 47·2 | 5·30 | .... | 5·27 | .... | 5·31 | .... | 6·13 |
| 8CaO | 224·0 | 25·14 | .... | 24·71 | .... | 25·22 | .... | 25·00 |
| $15SiO^2$ | 465·0 | 52·20 | .... | 52·13 | .... | 51·86 | .... | 53·90 |
| F—O | 10·7 | 1·20 | .... | 0·82 | | | | |
| 16HO | 144·0 | 16·16 | .... | 16·20 | .... | 16·91 | .... | 15·70 |
| | 890·9 | 100·00 | .... | 99·13 | .... | 99·30 | .... | 100·73 |

F—O represents hypothetical anhydrous fluoric acid, which, with one atom of CaO produces one atom of CaF. The formula of apophyllite is probably the following: $KO, 2SiO^2 + 6(CaO, 2SiO^2) + CaO, SiO^2 + CaF + 16Aq$.

¶ Rammelsberg regards the fluorine in apophyllite either as mechanically mixed, or possibly as replacing a portion of the oxygen. The formula which he gives for this mineral is: $KO, SiO^3 + 6(CaO, SiO^3) + 15HO$; or $2KO, 3SiO^2 + 3(2CaO, 3SiO^2) + 15HO$. (*Pogg.* 68, 506.) ¶

D. Silicate of Lime and Soda.—*Pectolite.* Occurs in fibrous masses with spherical surface; specific gravity 2·69. By gentle ignition, it becomes less brilliant and more friable. Before the blowpipe it fuses readily to a translucent glass, a few bubbles of gas being evolved. It dissolves with ease in borax, forming a clear glass; with microcosmic salt it yields a skeleton of silica. When it is introduced in small pieces into concentrated hydrochloric acid, several days elapse before decomposition takes place; it then becomes disintegrated and yields gelatinous silica. In the state of powder, it is more rapidly acted on; and in this case, the silica does not separate in the form of a jelly, but in viscid flakes. Pectolite, after ignition, and even after fusion, yields, when reduced to powder, a stiff jelly with hydrochloric acid. (Von Kobell, *Kastn. Arch.* 13, 385.)

| | *Pectolite.* | | | Von Kobell. |
|---|---|---|---|---|
| KO | | .... | .... | 1·57 |
| NaO | 31·2 | .... | 8·99 | .... 8·26 |
| 4CaO | 112·0 | .... | 32·26 | .... 33·77 |
| $6SiO^2$ | 186·0 | .... | 53·57 | .... 51·30 |
| 2HO | 18·0 | .... | 5·18 | .... 3·89 |
| Alumina with Sesquioxide of Iron | | .... | | .... 0·90 |
| | 347·2 | .... | 100·00 | .... 99·69 |

$NaO, 2SiO^2 + 4(CaO, SiO^2) + 2Aq$. A portion of the soda is replaced by potash. According to Berzelius, pectolite contains a small quantity of fluorine.

Related to this mineral is Walker's *Wollastonite*, which contains 5·55 per cent. of soda, 30·79 of lime, 2·59 of magnesia, 1·18 of sesquioxide of iron and alumina, 54·00 of silica, and 5·43 of water.

## Silicium and Magnesium.

A. Silicate of Magnesia.—*a. Disilicate.*—*α. Anhydrous.* 1. A mixture of 2 atoms of magnesia and one atom of silica exposed for two hours to the heat of a powerful wind-furnace, yields a milk-white, porous enamel. (Sefström.)

2. *Chrysolite* and *Olivine.* Often found in meteoric stones, as *Meteoric Olivine.* Crystalline system, the right prismatic. *Fig.* 75 with the *p*-surface, and also other forms: $i : t = 131° 29'$; $y : m = 141° 40'$; $t : u = 114° 6'$; $u : m = 155° 54'$; $u^1 : u = 131° 48'$; cleavage parallel to *t*. (Hauy.) Specific gravity from 3·33 to 3·44; harder than felspar; transparent, and generally of a yellowish green colour. Infusible before the blowpipe. Chrysolite is not decomposed by hydrochloric acid, but yields to sulphuric acid, without however forming a jelly. (Von Kobell, *J. pr. Chem.* 5, 214.) Powdered olivine is very readily decomposed by hydrochloric acid, yielding a jelly. (Berzelius, *Jahresbericht*, 15, 217.)

| | | | Stromeyer. *a.* | Stromeyer. *b.* | Walmstedt. *c.* | Berzelius. *d.* |
|---|---|---|---|---|---|---|
| 2MgO | 40 | 56·34 | 50·13 | 50·49 | 44·87 | 47·35 |
| FeO | | | 9·19 | 8·17 | 15·38 | 11·72 |
| $SiO^2$ | 31 | 43·66 | 39·73 | 40·09 | 40·16 | 40·86 |
| MnO | | | 0·09 | 0·20 | 0·10 | 0·43 |
| NiO | | | 0·32 | 0·37 | | |
| $Al^2O^3$ | | | 0·22 | 0·19 | 0·10 | |
| $SnO^2$ with CuO | | | | | | 0·17 |
| 2MgO, $SiO^2$ | 71 | 100·00 | 99·68 | 99·51 | 100·61 | 100·53 |

*a* is Oriental Chrysolite;—*b*, Olivine from the basalt of Vogelsberg;—*c*, Olivine from Somma;—*d*, Olivine accompanying the Siberian meteoric iron of Pallas.—Sometimes a smaller and sometimes a larger quantity of magnesia is replaced by protoxide of iron; and in *Hyalosiderite*—which moreover has the same crystalline form as chrysolite, and yields a jelly with hydrochloric acid—the oxide of iron, according to Walchner, amounts to 28·49 per cent.

*β. Hydrated.*—*Villarsite.*—Crystalline system, the right prismatic. *Fig.* 42; the obtuse angle of the rhombic base ($u^1 : u$) = 119° 59'.—Yellowish green and granular. (Dufrénoy, *Compt. Rend.* 14, 698.)

| | | *Villarsite.* | | | Dufrénoy. |
|---|---|---|---|---|---|
| 4MgO | 80·0 | ..... | 52·98 | ..... | 47·37 |
| $2SiO^2$ | 62·0 | ..... | 41·06 | ..... | 39·60 |
| HO | 9·0 | ..... | 5·96 | ..... | 5·80 |
| KO, 0·46; CaO, 0·53; | | MnO, 2·42; | | FeO, 3·59; | 7·00 |
| 2(2MgO, $SiO^2$) + Aq. | 151·0 | ..... | 100·00 | ..... | 99·77 |

*b. Two-thirds Silicate of Magnesia.*—*α. Bihydrated.*—*Noble Serpentine* or *Ophite* (together with *Marmalite, Picrolite* and *Variegated Asbestos* from Reichenstein).—*Serpentine:* a dense mineral, of specific gravity 2·5 to 2·6, and as hard as calcspar.—Translucent and generally of a green colour, with waxy lustre; unctuous to the touch. Heated in a tube, it evolves water and becomes opaque. Fuses before the blowpipe, chiefly at the edges, to a white enamel; with microcosmic salt it yields an infu-

sible skeleton of silica. Fuses, though with difficulty, with a small quantity of carbonate of soda; with a larger proportion of the latter, a swollen, infusible mass is produced. Exhibits a red colour when ignited with solution of cobalt. Pounded serpentine dissolves in concentrated hydrochloric acid, leaving a siliceous jelly; it is still more easily acted on by sulphuric acid, the silica being separated in the form of a viscid powder.—*Picrolite* is of a fibrous texture; in other respects, it possesses the same characters as serpentine.—*Variegated Asbestos* is fibrous and of a silky lustre. Before the blowpipe, only the finest fibres become rounded. It is easily and completely decomposed by concentrated hydrochloric acid, the silica remaining undissolved in the form of the fibres, and exhibiting a silky lustre. (Von Kobell.)

| | | | Hartwall. | Mosander. | Lychnell. | | |
|---|---|---|---|---|---|---|---|
| | | | *a.* | *b.* | *c.* | *d.* | *e.* |
| 3MgO | 60 | 42·86 | 41·66 | 44·20 | 40·64 | 42·41 | 41·25 |
| $2SiO^2$ | 62 | 44·28 | 42·97 | 42·34 | 41·95 | 41·58 | 41·67 |
| 2HO | 18 | 12·86 | 12·02 | 12·38 | 11·68 | 11·29 | 13·80 |
| FeO | | | 2·48 | 0·18 | 2·22 | 2·17 | 1·64 |
| $Al^2O^3$ | | | 0·87 | | 0·37 | trace. | |
| $CO^2$ | | | | 0·87 | 3·42 | 2·38 | 1·37 |
| | 140 | 100·00 | 100·00 | 99·97 | 100·28 | 99·83 | 99·73 |

| | Lychnell. | | Stromeyer. | Von Kobell. | Kühn. |
|---|---|---|---|---|---|
| | *f.* | *g.* | *h.* | *i.* | *k.* |
| MgO | 42·16 | 33·44 | 37·16 | 40·00 | 40·60 |
| $SiO^2$ | 42·16 | 40·98 | 41·66 | 43·50 | 44·48 |
| HO | 12·33 | 12·86 | 14·72 | 13·80 | 12·35 |
| FeO | 1·98 | 8·72 | 4·05 | 2·08 | 2·34 |
| $Al^2O^3$ | | 0·73 | | 0·40 | |
| $CO^2$ | 1·03 | 1·73 | MnO 2·25 | | |
| | 99·66 | 98·46 | 99·84 | 99·78 | 99·77 |

$3MgO, 2SiO^2 + 2Aq.$ or $2(MgO, SiO^2) + (MgO, 2Aq)$.

—*a*, is Noble Serpentine from Snarum;—*b*, from Gullsjö;—*c*, from Fahlun;—*d*, from Swärdsjö;—*e*, Marmalite from Hoboken;—*f*, ordinary Serpentine from Sala;—*g*, Picrolite from Taberg;—*h*, Picrolite from Philipstadt;—*i*, Variegated Asbestos from Reichenstein. ¶ *k*, Metaxite, a new mineral described by Kühn (*Ann. Pharm.* 59, 363), of the formula: $2(MgO + SiO^2 + \frac{1}{2}HO) + (MgO, HO)$. ¶ A portion of the magnesia is replaced by protoxide of iron, especially in picrolite. The presence of carbonic acid is due to an admixture of magnesite; in the amount of carbonic acid given under *c*, *d*, *e*, *f*, and *g*, bitumen is also included.

*β. Terhydrate.*—1. *Deweylite*, $3MgO, 2SiO^2 + 3Aq.$—Specific gravity = 2·2474; amorphous. (Thomson.)—2. *Hydrophite.*—$2MgO, FeO, 2SiO^2 + 3Aq.$ Specific gravity 2·65; soft, green, resembling serpentine, infusible before the blowpipe. (Svanberg, *Jahresber.* 20, 216.)

| | *Deweylite.* | | Thomson. |
|---|---|---|---|
| 3MgO | 60 | 40·27 | 40 |
| $2SiO^2$ | 62 | 41·61 | 40 |
| 3HO | 27 | 18·12 | 20 |
| | 149 | 100·00 | 100 |

| | | *Hydrophite.* | | Svanberg. |
|---|---|---|---|---|
| 2MgO | 40·0 | 24·36 | | 21·08 |
| MnO | | | | 1·66 |
| FeO | 35·2 | 21·44 | | 22·73 |
| $2SiO^2$ | 62·0 | 37·76 | | 36·19 |
| 3HO | 27·0 | 16·44 | | 16·08 |
| $Al^2O^3$ | | | | 2·89 |
| $VO^3$ | | | | 0·12 |
| | 164·2 | 100·00 | | 100·75 |

*c. Three-fourths Silicate of Magnesia.—Hydrated.—a. Antigorite* consists of $4MgO, 3SiO^2 + Aq.$ or more accurately, inasmuch as a portion of the magnesia is replaced by protoxide of iron, $(10MgO, 2FeO + 9SiO^2) + 3Aq.$ (*Vid.* Schweizer, *Pogg.* 49, 595.)

*b. Schiller-spar* appears to be composed of $4MgO, 3SiO^2 + 3Aq.$ or $MgO, 3Aq. + 3(MgO, SiO^2)$; in this mineral, also, a large proportion of the magnesia is replaced by protoxide of iron, protoxide of manganese, and lime. (*Vid.* Köhler, *Pogg.* 11, 192.)

*d. Monosilicate of Magnesia.—α. Anhydrous.*—1. A mixture of one atom of magnesia with one atom of silica exposed for a couple of hours to the heat of a powerful wind-furnace, yields a nearly white enamel, of pearly lustre and highly crystalline. (Sefström.)

2. The *Asbestos of Koruk*, examined by Lappe (*Pogg.* 35, 486), and Thomson's bisilicate of magnesia appear to have this composition.

| | | | | Lappe. | | Thomson. |
|---|---|---|---|---|---|---|
| MgO | 20 | 39·22 | | 31·38 | | 36·52 |
| $SiO^2$ | 31 | 60·78 | | 58·48 | | 56·64 |
| CaO | | | | 0·04 | | |
| FeO | | | | 9·22 | $Fe^2O^3$ | 2·46 |
| MnO, CaO, $Al^2O^3$, $PO^5$ | | | | 0·88 | $Al^2O^3$ | 6·07 |
| $MgO, SiO^2$ | 51 | 100·00 | | 100·00 | | 101·69 |

*β. Hydrated.*—1. *Picrosmine.*—Crystalline system, the right prismatic; not found in crystals, but corresponding in its cleavage-planes to *Fig.* 74; cleavage distinct parallel to *m*; less distinct parallel to *t*, *u* and *i*; $i : i = 117° 49'$; $u' : u = 53° 8'$. The cleavage-surfaces parallel to *m* are of a pearly lustre, the others glassy. The mineral itself is of a pale greenish grey colour, and transparent at the edges; somewhat softer than calc-spar; specific gravity 2·66. (Haidinger). When ignited it evolves water, becoming black at first, but subsequently white. Picrosmine does not fuse before the blowpipe, but increases in density. It dissolves in borax, and also in microcosmic salt, leaving, however, a skeleton of silica in the latter case; with carbonate of soda, it yields a turbid, semi-fused mass; when it is ignited with a solution of cobalt, a red colour is produced. (Magnus, *Pogg.* 6, 53.)

| | | | Magnus. *Picrosmine.* |
|---|---|---|---|
| 2MgO | 40 | 36·04 | 33·35 |
| $2SiO^2$ | 62 | 55·85 | 54·89 |
| HO | 9 | 8·11 | 7·30 |
| MnO | | | 0·42 |
| $Fe^2O^3$ | | | 1·40 |
| $Al^2O^3$ | | | 0·79 |
| $2MgO, SiO^2 + Aq.$ | 111 | 100·00 | 98·15 |

2. *Picrophyll* and *Aphrodite* or *Meerschaum of Longbanshyttan. Picrophyll:* dense; laminated; of specific gravity 2·73; softer than calc-spar; iridescent; of a dark greyish green colour; resembling serpentine in appearance. It yields water on ignition, and becomes white, without however losing its lustre. Infusible before the blowpipe; ignited with cobalt solution, it assumes a dingy red tint. (Svanberg, *Pogg.* 50, 662.)

| | | | Svanberg. *Picrophyll.* | | Berlin. *Aphrodite.* |
|---|---|---|---|---|---|
| CaO | | | 0·78 | | |
| 3MgO | 60 | 35·09 | 30·10 | | 33·72 |
| MnO | | | trace. | | 1·62 |
| FeO | | | 6·86 | | 0·59 |
| $3SiO^2$ | 93 | 54·38 | 49·80 | | 51·55 |
| 2HO | 18 | 10·53 | 9·83 | | 12·32 |
| $Al^2O^3$ | | | 1·11 | | 0·20 |
| $3(MgO,SiO^2)+2Aq$ | 171 | 100·00 | 98·48 | | 100·00 |

On account of the larger amount of water which it contains, Berlin considers aphrodite as $4(MgO,SiO^2)+3Aq$. ¶ Kühn (*Ann. Pharm.* 59, 363,) gives the analysis of a sesquihydrate of silicate of magnesia under the name of *Kerolite.*

| | *Kerolite.* | | | Kühn. |
|---|---|---|---|---|
| 2MgO | 40 | | 31·50 | 31·26 |
| $2SiO^2$ | 62 | | 47·46 | 46·96 |
| 3HO | 27 | | 21·04 | 21·22 |
| $2(MgO,SiO^2)+3Aq.$ | 129 | | 100·00 | 99·44 |

*Neolite.*—3RO, $2SiO^3$ or $3(RO,SiO^2)$.—Described by Scheerer (*Pogg.* 71, 285) as a *Talc* in which a portion of the silica is replaced by alumina.—Found in the Aslak iron mines, near Arendal in Norway, occurring either in small crystalline laminæ and threads arranged in tufts; or in an apparently amorphous state spread over the surface, from a few lines to an inch in thickness. The crystallized variety is nearly as hard as talc, but the amorphous variety is softer. It is unctuous to the touch, and may be cut like soap. Its colour is brownish and blackish green, passing almost into black; it varies from a fatty to a silky lustre; its specific gravity, when perfectly dry, is 2·77. At a temperature of 100°, it loses a considerable quantity of hygroscopic water—especially the amorphous variety—and acquires a lighter colour, sometimes almost approaching to white. The dried mineral evolves air-bubbles when immersed in water, and re-absorbs the water with so much rapidity, that it falls to pieces shortly after immersion. The following is the composition of two specimens given by Scheerer.

| | *Neolite.* (1) | | (2) |
|---|---|---|---|
| CaO | 0·28 | | 0·00 |
| MgO | 31·24 | | 24·73 |
| FeO | 3·79 | | 7·92 |
| MnO | 0·89 | | 2·64 |
| $Al^2O^3$ | 7·33 | | 10·27 |
| $SiO^3$ | 52·28 | | 47·35 |
| HO | 4·04 | | 6·28 |
| | 99·85 | | 99·19 |

The proportion of oxygen in the acid to that in the other constituents follows:

| | $SiO^3$. | | $Al^2O^3$. | | RO. | | HO. |
|---|---|---|---|---|---|---|---|
| 1. | 8 | | 1 | | 4 | | 1 |
| 2. | 5 | | 1 | | $2\frac{1}{2}$ | | $1\frac{1}{2}$ |

RO represents the sum of the oxygen in the magnesia, the ferrous and manganous oxides, and the lime. From this it must be evident that the two analyses cannot be brought under one formula by the ordinary method of calculation; but if we reckon the alumina as an electro-negative element together with the silica, and the water as an electro-positive element with the magnesia, &c. in the isomeric proportions of $3Al^2O^3 = 2SiO^3 (= 3SiO^2)$, and $3HO = 1MgO$ (*vid.* I., 93), the following results are obtained:

| | $SiO^3$. | | RO. |
|---|---|---|---|
| 1. | 29·43 | | 14·75 |
| 2. | 27·78 | | 14·05 |

or nearly 2 : 1, from which the formula $3RO, 2SiO^3$ (or $RO, SiO^2$) may be deduced. ¶

*e. Five-fourths Silicate of Magnesia.—Talc* occurs in rhombic and six-sided tabular crystals; $u^1 : u = 120°$ nearly; cleavage distinct, parallel to the base; specific gravity = 2·65 to 2·74; softer than gypsum; unctuous to the touch; of a pearly lustre at the fractured surfaces; translucent. Splits up into laminæ before the blowpipe, and hardens without fusing. With microcosmic salt it yields a turbid glass, together with an insoluble skeleton of silica. With a small quantity of carbonate of soda it forms a semifused slag, but with a larger proportion, a transparent glass. Solution of cobalt imparts a pale flesh-colour to it. Neither before nor after ignition is it acted on, to any visible extent, by hydrochloric acid or oil of vitriol.

| | *Talc.* | | | Von Kobell. *a.* | Von Kobell. *b.* | | Klaproth. *c.* | | Wackenroder. *d.* |
|---|---|---|---|---|---|---|---|---|---|
| 4MgO | 80 | 34·04 | .... | 32·4 | 31·92 | .... | 30·50 | .... | 33·03 |
| $5SiO^2$ | 155 | 65·96 | .... | 62·8 | 62·80 | .... | 62·00 | .... | 61·97 |
| FeO | | | .... | 1·6 | 1·10 | $Fe^2O^3$ | 2·50 | .... | 0·74 |
| $Al^2O^3$ | | | .... | 1·0 | 0·60 | KO | 2·75 | | |
| HO | | | .... | 2·3 | 1·92 | .... | 0·50 | .... | 3·48 |
| | 235 | 100·00 | .... | 100·1 | 98·34 | .... | 98·25 | .... | 99·22 |

This mineral may be regarded as $2(MgO, SiO^2) + (2MgO, 3SiO^2)$.—*a* is talc from Greiner;—*b* from Proussiansk in Siberia;—*c* is laminar talc from Gotthard; the protoxide of iron in *a* and *b* is also mixed with oxide of titanium; *d* is from a specimen of Chinese sculpture, of specific gravity 2·747, and having a dull, uneven, splintered fracture; pale red, translucent, becoming black before the blowpipe at first, but afterwards white and hard, and fusing slightly at the edges. It dissolves slowly in borax, forming a clear bead, and with difficulty in phosphate of soda, leaving an insoluble skeleton of silica; with carbonate of soda it swells up and forms an opaque slag. This substance is powerfully attacked both by hydrochloric and sulphuric acid, but the decomposition is incomplete [by this character it is distinguished from ordinary talc]. (Wackenroder.)

*f. Four-thirds Silicate of Magnesia.—Steatite.*—Dense; of uneven, splintered fracture; specific gravity 2·6; soft and unctuous to the touch; slightly translucent. Before the blowpipe, it fuses at the edges to a white enamel; when ignited with solution of cobalt, it assumes a pale red colour. Not decomposed by acids.

| | | | Lychnell. | | | |
|---|---|---|---|---|---|---|
| | *Steatite.* | | *a.* | *b.* | *c.* | *d.* |
| 3MgO ..... | 60 | 32·61 | 33·42 | 30·23 | 27·70 | 34·30 |
| $4SiO^2$ ..... | 124 | 67·39 | 66·53 | 66·70 | 64·53 | 63·13 |
| KO ..... | | | | | | |
| FeO ..... | | | trace. | 2·41 | 6·85 | 2·27 |
| $Al^2O^3$ ..... | | | | | | |
| HO ..... | | | | | | |
| | 184 | 100·00 | 99·95 | 99·34 | 99·08 | 99·70 |

$MgO, SiO^2 + 2MgO, 3SiO^2$.—*a* is Steatite from China,—*b* from Mont Caunegon,—*c* from Scotland,—*d* from Sala.

*g. Sesquisilicate of Magnesia.*—*α. Anhydrous.*—A mixture of 2 atoms of magnesia with 3 atoms of silica yields, after two hours' exposure to the heat of a powerful blast-furnace, an enamel similar to that obtained with equal numbers of atoms (III., 397), excepting that it is more crystalline, and does not fuse so completely. (Seftström.)

*β. Hydrated.—Meerschaum.*—Amorphous; porous; specific gravity from 1·3 to 1·6; fracture, earthy; soft, tenacious, and opaque. It evolves water on ignition: shrinks up before the blowpipe and becomes hard, fusing at the edges to a white enamel. When ignited with cobalt solution, it assumes a pale-red colour. The mineral is decomposed by hydrochloric acid with separation of silica in viscid flakes. According to Döbereiner (*J. pr. Chem.* 17, 157), meerschaum deprived, by very gentle heating, of its water of hydration, gives out a considerable quantity of heat when dipped for a short time into cold water; and moreover, rapidly absorbs from the air the water which it has lost; but not after strong ignition.

According to the same authority, artificial meerschaum is obtained as a light, strongly coherent mass, yielding to the knife, by precipitating a very dilute solution of sulphate of magnesia with sesquisilicate of potash, washing the pasty precipitate for a considerable time, and drying it in the air.

| | | | Lychnell. | Berthier. | | | Tennant. |
|---|---|---|---|---|---|---|---|
| | *Meerschaum.* | | *a.* | *b.* | *c.* | *d.* | *e.* |
| 2MgO..... | 40 | 26·49 | 27·80 | 25 | 23·8 | 24·0 | 23·65 |
| $3SiO^2$ ..... | 93 | 61·59 | 60·87 | 50 | 53·8 | 54·0 | 50·70 |
| 2HO ..... | 18 | 11·92 | 11·29 | 25 | 20·0 | 20·0 | 20·60 |
| $Fe^2O^3$ ..... | | | 0·09 | | 1·2 | | FeO 1·70 |
| $Al^2O^3$ ..... | | | | | | 1·4 | 3·55 |
| | 151 | 100·00 | 100·05 | 100 | 98·8 | 99·4 | 100·20 |

$2MgO, 3SiO^2 + 2Aq$.—*a* and *b* are specimens of meerschaum from the Levant,—*c* from Cabanas,—*d* from Coulomiers,—*e* is Thomson's magnesite. The analyses *b* to *e* give 4 instead of 2 atoms of water; Döbereiner also found 4 atoms. Lychnell had previously freed the meerschaum from mechanically combined water by drying it in vacuo over oil of vitriol.

B. Fluoride of Silicium and Magnesium.—A solution of magnesia in hydrofluosilicic acid yields on evaporation a transparent, yellowish, gummy mass, easily soluble in water. (Berzelius.)

| | Calculation. | | |
|---|---|---|---|
| Mg ..... | 12·0 | .... | 14·44 |
| Si ..... | 15·0 | .... | 18·05 |
| 3F ..... | 56·1 | .... | 67·51 |
| $MgF, SiF^2$ ..... | 83·1 | .... | 100·00 |

C. Silicate of Magnesia with Fluoride of Magnesium.—*Chondrodite.*—Crystalline system, the oblique prismatic. *Fig.* 85, without the *i* and *f*-faces; *i* : the edge between $u^1$ and $u = 112° 12'$; $u^1 : u = 147° 48'$; $\alpha : t = 101° 30'$; $\alpha : \alpha = 157°$; $\alpha : u^1$ or $u = 161° 44'$; $t : u^1 = 106° 6'$; cleavage parallel to *i*, and less distinct parallel to *m* and *t*. (Hauy.) Specific gravity from 3·12 to 3·19; harder than felspar. When strongly heated in the blowpipe-flame, it evolves hydrofluoric acid and fuses at the edges. With microcosmic salt it yields hydrofluoric acid and an insoluble skeleton of silica; with borax, a clear glass after a long time; but by interrupted blowing or *flaming*, the glass becomes opaque and crystalline. With a small proportion of carbonate of soda, a difficultly fusible, greyish slag is obtained; but with a larger quantity, a blistered infusible mass. It acquires a slight red tinge when ignited with solution of cobalt, provided the quantity of iron present is not too great. Oil of vitriol decomposes it completely, with evolution of gaseous fluoride of silicium. It dissolves in hydrochloric acid, with separation of gelatinous silica.

| | | | Rammelsberg. | | | Thomson. |
|---|---|---|---|---|---|---|
| | *Chondrodite.* | | *a.* | *b.* | *c.* | *d.* |
| 8MgO | 160·0 | 60·68 | 56·12 | 56·61 | 54·50 | 54·64 |
| $3SiO^2$ | 93·0 | 35·27 | 33·51 | 33·10 | 33·10 | 36·00 |
| F—O | 10·7 | 4·05 | 4·30 | 4·97 | 6·75 | 3·75 |
| FeO | | | 3·57 | 2·35 | 5·54 | 3·97 |
| HO | | | | | | 1·62 |
| | 263·7 | 100·00 | 97·50 | 97·03 | 99·89 | 99·98 |

Probably arranged as: $3(2MgO, SiO^2) + (MgO, MgF.)$—A portion of the magnesia is replaced by protoxide of iron;—*a* is yellow Chondrodite from North America;—*b*, a yellow specimen from Pargas;—*c*, a grey variety from Pargas;—*d*, a reddish yellow variety from Eden near New York.

D. Silicate of Magnesia and Lime.—*a. Bibasic.*—*α.* Many furnace-slags having the crystalline form of olivine, contain one atom of silicic acid to 2 atoms of magnesia and lime. (Mitscherlich, *Ann. Chim. Phys.* 24, 355.) A mixture of one atom of lime, one atom of magnesia, and one atom of silica exposed for two hours to the heat of a forge, yields a thoroughly fused, pale bluish-green glass, with a granulated fracture. (Sefström.)—Lime, magnesia, and silica in equal parts fuse to a greenish glass, which emits sparks when struck with steel. If the proportion of lime be increased, the fusibility remains nearly the same; with a larger proportion of silica, it is less; and excess of magnesia renders the mixture infusible. (Achard.)

*β. Batrachite.*—Fusible before the blowpipe; with microcosmic salt it yields a skeleton of silica; it is but feebly acted on by acids. (Rammelsberg, *Pogg.* 51, 446.)

| | *Batrachite.* | | Rammelsberg. |
|---|---|---|---|
| 2CaO | 56 | 35·44 | 35·45 |
| 2MgO | 40 | 25·32 | 21·79 |
| FeO | | | 2·99 |
| $2SiO^2$ | 62 | 39·24 | 37·69 |
| HO | | | 1·27 |
| | 158 | 100·00 | 99·19 |

$2CaO, SiO^2 + 2MgO, SiO^2$. A portion of magnesia is replaced by protoxide of iron.

*b. Monosilicate of Magnesia and Lime.*—*α.* When one atom of lime is fused with one atom of magnesia and 2 atoms of silica, or one atom of lime with 2 atoms of magnesia and 6 atoms of silica, and the mass very slowly cooled, it crystallizes in the form of augite. The first mixture yields a mass resembling ordinary augite; the latter, a mass like augite from Finland. (Berthier, *Ann. Chim. Phys.* 24, 376.)—In the cavities of a slag from an iron-furnace fed with a hot-air blast, Nöggerath (*J. pr. Chem.* 20, 501) found artificial crystals of augite.—Sefström exposed the three earths in the following proportions to the heat of a powerful wind-furnace, and obtained the annexed results in well fused masses; $CaO,SiO^2 + MgO,SiO^2$: opaline glass, crystalline in some parts; $CaO,SiO^2 + 2(MgO,SiO^2)$: enamel, crystalline in some parts; $2(CaO,SiO^2) + MgO,SiO^2$: opalescent glass, with granulated fracture.

*β. Augite.*—Crystalline system, the oblique prismatic. *Fig.* 99 with the *t*-face; *Fig.* 103, 106, and numerous other forms; $i : t = 106° 6'$; $i : a = 150°$; $u : u^1 = 87° 42'$; $t : u$ or $u^1 = 133° 51$; $m : u$ or $u^1 = 136° 9'$; cleavage parallel to $u$ and $u^1$, and less distinct parallel to $m$ and $t$. (Hauy.) Specific gravity from 3·2 to 3·5; hardness between apatite and felspar. Fuses with various degrees of facility according to its composition. Diopside yields a colourless, almost transparent glass; ferruginous augite, a dark coloured glass. Augite dissolves readily in borax, but with difficulty in microcosmic salt, forming a skeleton of silica. It is scarcely attacked by hydrochloric acid.

| | | | Wackenroder. | Bonsdorff. | H. Rose. | |
|---|---|---|---|---|---|---|
| | | | *a.* | *b.* | *c.* | *d.* |
| CaO | 28 | 25·46 | 24·74 | 24·76 | 23·57 | 24·94 |
| MgO | 20 | 18·18 | 18·22 | 18·55 | 16·49 | 18·00 |
| MnO | | | 0·18 | 0·32 | 0·42 | 2·00 |
| FeO | | | 2·50 | 0·99 | 4·44 | 1·08 |
| $2SiO^2$ | 62 | 56·36 | 54·16 | 54·83 | 54·86 | 54·64 |
| $Al^2O^3$ | | | 0·20 | 0·28 | 0·21 | |
| | 110 | 100·00 | 100·00 | 99·73 | 99·99 | 100·66 |

*a* is Diopside from Fassa;—*b*, from Tammare;—*c*, Salite, from Sala;—*d*, Malacolite, from Orrijerfvi.

In the following specimens of augite, the magnesia is replaced, sometimes about half, and sometimes almost wholly, by protoxide of iron.

| | Calculation. | | H. Rose. |
|---|---|---|---|
| | | | *a.* |
| 2CaO | 56·0 | 23·81 | 23·47 |
| MgO | 20·0 | 8·50 | 11·49 |
| MnO | | | 0·61 |
| FeO | 35·2 | 14·97 | 10·02 |
| $4SiO^2$ | 124·0 | 52·72 | 54·08 |
| | 235·2 | 100·00 | 99·67 |

| | | Calculation. | H. Rose. | Berzelius. |
|---|---|---|---|---|
| | | | *b.* | *c.* |
| CaO | 28·0 | 22·37 | 20·87 | 20·00 |
| MgO | | | 2·98 | 4·50 |
| MnO | | | trace. | 3·00 |
| FeO | 35·2 | 28·11 | 26·08 | 18·85 |
| $2SiO^2$ | 62·0 | 49·52 | 49·01 | 50·00 |
| | 125·2 | 100·00 | 98·94 | 96·35 |

*a* is Malacolite from Dalecarlia.—*b*, Hedenbergite from Tunaberg.—*c*, reddish brown Malacolite from Dagerö.

*Aluminous Augite.*—The alumina probably exists in the mineral as a garnet-compound ($3MgO, Al^2O^3, 3SiO^2$, for example), mixed with the augite*.

| | | | Kudernatsch. | | | |
|---|---|---|---|---|---|---|
| | | | *a.* | *b.* | *c.* | *d.* |
| 6CaO | 168·0 | 21·60 | 18·90 | 22·96 | 22·29 | 19·57 |
| 6MgO | 120·0 | 15·43 | 16·91 | 14·43 | 13·01 | 13·48 |
| FeO | 35·2 | 4·53 | 7·26 | 6·25 | 7·96 | 12·04 |
| $Al^2O^3$ | 51·4 | 6·61 | 6·47 | 5·37 | 4·85 | 4·02 |
| $13SiO^2$ | 403·0 | 51·83 | 50·73 | 50·90 | 50·55 | 50·15 |
| | 777·6 | 100·00 | 100·27 | 99·91 | 98·66 | 99·26 |

The composition is therefore about $(6CaO, 3MgO, FeO, 10SiO^2) + (3MgO, Al^2O^3, 3SiO^2)$, that is to say, 5 atoms of augite to 1 atom of garnet. *a* is ordinary Augite from the Rhone; *b*, from Vesuvius; *c*, from Etna; *d*, from Fassa. The composition of the latter, which is richer in protoxide of iron and poorer in alumina, may be expressed by the following formula: $(9CaO, 5MgO, 4FeO, 18SiO^2) + (3MgO, Al^2O^3, 3SiO^2)$; that is to say, 9 atoms of augite to 1 atom of garnet.

*Diallage* or *Bronzite* also contains 1 atom of silica to each atom of base, consisting of lime, magnesia, protoxide of manganese, and protoxide of iron, in variable proportions; moreover, there is generally present from 1 to 4 per cent. of alumina, and $\frac{1}{2}$ to 4 per cent. of water. These last-mentioned ingredients appear to exist, sometimes in the form of hydrated silicate of alumina ($Al^2O^3, 2SiO^2, 2Aq.$), sometimes in the form of hydrate of alumina, as the following arrangement of the calculations will show:

| | | *Diallage.* | | Köhler. | | |
|---|---|---|---|---|---|---|
| | | | | *a.* | | *b.* |
| 11CaO | 30[illegible] | 17·02 | .... | 17·06 | .... | 19·09 |
| 15MgO | [illegible] | 16·57 | .... | 17·55 | .... | 14·91 |
| 4FeO | 140·8 | 7·78 | .... | 8·08 | .... | 8·67 |
| MnO | | | | | .... | 0·38 |
| $32SiO^2$ | 992·0 | 54·80 | .... | 53·71 | .... | 53·20 |
| $Al^2O^3$ | 51·4 | 2·84 | .... | 2·82 | .... | 2·47 |
| 2HO | 18·0 | 0·99 | .... | 1·04 | .... | 1·77 |
| | 1810·2 | 100·00 | .... | 100·26 | .... | 100·49 |

* ¶ The following theory of Bonsdorff, that in aluminous augites, and likewise in amphibolites, &c. (pp. 405—408), a portion of silica may very possibly be replaced by alumina, in the proportion of $2SiO^3 : 3Al^2O^3$ (or $SiO^2 = Al^2O^3$), is confirmed by Scheerer (*Pogg.* 70, 545). The theory is principally based upon the fact, that by adding two-thirds of the oxygen of the alumina to that of the silica to form the electro-negative element, and comparing it with the oxygen of the electro-positive element, the proportions obtained are very near to the numbers 27·81 : 13·90, which correspond to the formula $3RO, 2SiO^3$. This analogy may be traced by the analyses through a great many species of augite, besides Diallage, Paulite, and Gedrite (a mineral discovered by Dufrénoy in the Pyrenees, and resembling Paulite or Hypersthene.) In the case of Hornblende and allied minerals, the proportions are 28·5 : 13, or by calculation, 28·5 : 12·7, which corresponds to the formula $RO, SiO^2 + 3RO, 2SiO^3$. The objection to this theory lies in the fact that talc, the formula of which is $3RO, 2SiO^3$, crystallizes in rhombic prisms, while spinelle, with the formula $RO, Al^2O^3$ or $3RO, 3Al^2O^3$, forms regular octohedrons. Scheerer, in remarking on this fact, denies that it is inconsistent with the above view, but does not state the grounds on which his conclusion is based. ¶

| | | Diallage. | | | Köhler. c. | | Köhler. d. |
|---|---|---|---|---|---|---|---|
| 1CaO | 28·0 | .... | 2·38 | .... | 1·30 | .... | 2·19 |
| 18MgO | 360·0 | .... | 30·63 | .... | 32·67 | .... | 29·68 |
| 3FeO | 105·6 | .... | 8·98 | .... | 7·46 | .... | 8·46 |
| MnO | | .... | | .... | 0·35 | .... | 0·62 |
| $22SiO^2$ | 682·0 | .... | 58·01 | .... | 57·19 | .... | 56·81 |
| $Al^2O^3$ | | .... | | .... | 0·70 | .... | 2·07 |
| HO | | .... | | .... | 0·63 | .... | 0·22 |
| | 1175·6 | .... | 100·00 | .... | 100·30 | .... | 100·05 |

*a*, is Diallage from the Gabbro of Baste; *b*, from the Gabbro of Prato, near Florence; *c*, from the basalt of Stempel, near Marburg; *d*, from the Seefeld Alp in the Tyrol. The approximate formula for *a* and *b* is: $30(CaO, MgO, FeO)30SiO^2 + Al^2O^3, 2SiO^2 + 2Aq.$; in that for *c* and *d*, alumina and water are not taken into account. Diallage from the Euphotide of Corsica appears, according to Boulanger's analysis, to consist of $5(CaO, MgO, MnO, FeO), 5SiO^2 + MgO, Al^2O^3, 2Aq.$; that is to say, a mixture of 5 atoms of augite and 1 atom of a variety of spinelle containing 2 atoms of water.

*Hypersthene* or *Paulite* has likewise a composition corresponding to that of augite.

¶ A mineral closely related to Bronzite, and containing vanadium, has been examined by Schafhäutl, and named *Vanadic Bronzite*. It is found at Bracco in the steatite formation on the coast of Genoa, and occurs in tolerably large laminæ, with one very distinct, and two less defined cleavage planes. Its fracture is somewhat curved and broken; it has a mother-of-pearl lustre; is translucent in thin plates, and of a greenish grey colour. Somewhat less hard than felspar, and easily broken. When treated with dilute hydrochloric acid, it acquires a light apple-green colour. Sp. gr. = 3·255. When exposed to the blowpipe flame in thin laminæ, it separates lengthwise into threads, and, in the outer flame, fuses at the edges; in the inner flame, it emits a bright light, and melts to a brown bead. With borax, on platinum wire, it fuses to a glass which is yellow while hot, and remains yellow on cooling, if tolerably saturated; in the inner flame, a yellow glass is produced, which becomes bluish green on cooling, and again changes to yellow in the outer flame. With microcosmic salt, in the outer flame, silica is separated, and a yellow glass obtained, the colour of which disappears as it cools; a similar result is obtained in the inner flame, excepting that the glass sometimes becomes greenish on cooling.

| | Schafhäutl. Vanadic Bronzite. | | Schafhäutl. Ordinary Bronzite. |
|---|---|---|---|
| CaO | 18·13 | ..... | 18·28 |
| MgO | 14·12 | ..... | 15·69 |
| FeO | 3·23 | | |
| VnO | 3·65 | FeO .... | 8·23 |
| NaO | 3·75 | | |
| $SiO^3$ | 49·50 | ..... | 51·34 |
| $Al^2O^3$ | 5·55 | ..... | 4·39 |
| HO | 1·77 | ..... | 2·11 |
| | 99·70 | ..... | 100·04 |

The formula of Vanadic Bronzite is not given by Schafhäutl; but if $SiO^2$ is adopted instead of $SiO^3$, it will [illegible]ly resemble that of ordinary

Bronzite, in which part of the protoxide of iron is replaced by oxide of vanadium and soda. (*Ann. Pharm.* 51, 254.) ¶

*c. Six-fifths Silicate of Magnesia and Lime.—Hornblende, Amphibole.* Crystalline system, the oblique prismatic. Primary form, *Fig.* 81, together with other forms, especially with the faces *m*, *t*, *α*, *h*, *f*; $i : u^1$ or $u = 106° 55'$; $i : m$ (or the edge between $u^1$ and $u$) $= 104° 57'$; $\alpha : t = 105° 11'$; $h : t = 105° 11'$; $u^1 : u = 124° 34'$; $u : m = 152° 17'$; $u : t = 117° 43'$. Cleavage distinct parallel to $u^1$ and $u$; less distinct parallel to *m* and *t*. (Hauy.) Hardness between apatite and felspar. Swells up when heated, and fuses with various degrees of facility (the more magnesia there is present, the higher is the temperature required), forming a colourless, or if it contains iron, a coloured glass. It sometimes resists the action of hydrochloric and sulphuric acids; at other times, when iron is present, it is slightly decomposed by them.

It may in general be regarded as $3(MO, SiO^2) + 2MO, 3SiO^2$. The symbol MO denotes a mixture in variable proportions of lime, magnesia, protoxide of iron, and protoxide of manganese. Fluoride of calcium also is generally present in small and variable quantities, and therefore most probably in a state of mechanical mixture. Many varieties of hornblende likewise contain alumina, probably in the form of $MgO, Al^2O^3$, or $FeO, Al^2O^3$, or a mixture of the two; in short, mixed in variable proportions with the hornblende, in the form of a compound analogous to spinelle or zeilanite. At all events, when the quantities of the different substances found by analysis are divided by their atomic weight, so as to obtain the atomic numbers (I., 52) and from the atomic numbers of the stronger bases (CaO, MgO, MnO, FeO) a quantity equal to the atomic number of the hypothetically anhydrous fluoric acid and of the alumina is deducted, the remaining atomic number of the stronger bases is to that of the silicic acid, for the most part, as 5 : 6.

*α. Tremolite, Grammatite.* Specific gravity = 2·93; swells up on exposure to heat, and fuses with difficulty to a colourless glass.

*β. Actynolite.* (*Strahlstein.*) Specific gravity = 3·03. Coloured green by chromium and iron.

| | At. | *Tremolite.* | | Bonsdorff. *a.* | *b.* |
|---|---|---|---|---|---|
| CaO | 6 | 168·0 | 13·74 | 12·73 | 14·11 |
| MgO | 15 | 300·0 | 24·53 | 24·31 | 25·00 |
| FeO | | | | 1·00 | 0·50 |
| MnO | | | | 0·47 | |
| $SiO^2$ | 24 | 744·0 | 60·85 | 60·10 | 59·75 |
| F—O | 1 | 10·7 | 0·88 | 0·83 | 0·94 |
| $Al^2O^3$ | | | | 0·42 | trace. |
| HO | | | | 0·15 | 0·10 |
| | | 1222·7 | 100·00 | 100·01 | 100·40 |

| | At. | *Actynolite.* | Bonsdorff. *c.* |
|---|---|---|---|
| CaO | 5·5 | 14·02 | 14·25 |
| MgO | 11·5 | 20·94 | 21·10 |
| FeO | 1·5 | 4·81 | 3·95 |
| MnO | | | 0·31 |
| $SiO^2$ | 21·0 | 59·26 | 59·75 |
| F—O | | 0·97 | 0·76 |
| | | 100·00 | 100·12 |

*a* is Tremolite from Fahlun;—*b*, from Gullsjö;—*c* is Actynolite from Taberg. The calculation for tremolite *a*, gives 6+15 = 21 atoms of base; and if from this we subtract one atom for the hypothetically anhydrous fluoric acid, there remain 20 atoms of base to 24 atoms of silicic acid = 5 : 6. In actynolite, the atoms of base amount to 5·5+11·5+1·5 = 18·5, and after the subtraction of one atom for the hydrofluoric acid there remain 17·5 atoms, which are combined with 21 atoms of silicic acid; 17·5 : 21=5 : 6.

*γ. Anthophyllite.* Specific gravity, 3·12; fuses with great difficulty to a blackish grey glass,—not decomposed by acids.

| | At. | *Anthophyllite.* | | L. Gmelin. *Fahlun.* | Vopelius. *Kongsberg.* | Thomson. *Perth.* |
|---|---|---|---|---|---|---|
| CaO | 1 | 28·0 | 1·73 | 2 | | 3·55 |
| MgO | 18 | 360·0 | 22·28 | 23 | 24·35 | 29·30 |
| MnO | 1 | 35·6 | 2·20 | 4 | 2·38 | |
| FeO | 6 | 211·2 | 13·07 | 13 | 13·94 | 2·10 |
| $SiO^2$ | 30 | 930·0 | 57·54 | 56 | 56·74 | 57·60 |
| $Al^2O^3$ | 1 | 51·4 | 3·18 | 3 | | 3·20 |
| HO | | | | | 1·67 | 3·55 |
| | | 1616·2 | 100·00 | 101 | 99·08 | 99·30 |

If from the 26 atoms of base, one atom be subtracted for the alumina, there will remain 25 atoms of base to 30 atoms of silica = 5 : 6; but the analyses give rather too small a quantity of silicic acid for this calculation.

*δ. Common Hornblende.* Specific gravity 3·0 to 3·4. Dark green; readily swelling up and fusing to a dark glass. Distinguished by the presence of a large amount of protoxide of iron and a compound containing alumina. It may be regarded as 5(CaO; MgO; FeO; MnO), $6SiO+xCaF+xMgO, Al^2O^3$ or FeO, $Al^2O^3$. This formula is substantiated by the annexed calculations, in which also the fluorine is taken into account.

| | At. | *Tremolite.* | | Bonsdorff. *a.* |
|---|---|---|---|---|
| CaO | 5 | 140·0 | 12·72 | 12·73 |
| MgO | 12 | 240·0 | 21·80 | 21·86 |
| FeO | 1 | 35·2 | 3·19 | 2·28 |
| MnO | | | | 0·57 |
| $SiO^2$ | 16·8 | 520·8 | 47·31 | 47·21 |
| $Al^2O^3$ | 3 | 154·2 | 14·01 | 13·94 |
| F—O | 1 | 10·7 | 0·97 | 0·90 |
| HO | | | | 0·44 |
| | | 1100·9 | 100·00 | 99·93 |

| | At. | *Common Hornblende.* | | Bonsdorff. *b.* |
|---|---|---|---|---|
| CaO | 3·2 | 89·6 | 13·19 | 13·83 |
| MgO | 6·4 | 128·0 | 18·84 | 18·79 |
| FeO | 1·5 | 52·8 | 7·77 | 7·32 |
| MnO | | | | 0·22 |
| $SiO^2$ | 10·2 | 316·2 | 46·53 | 45·69 |
| $Al^2O^3$ | 1·6 | 82·2 | 12·10 | 12·18 |
| F—O | 1 | 10·7 | 1·57 | 1·50 |
| | | 679·5 | 100·00 | 99·53 |

| | At. | | *Common Hornblende.* | | | | Bonsdorff. *c.* |
|---|---|---|---|---|---|---|---|
| CaO | 9 | .... | 252·0 | .... | 9·82 | .... | 10·16 |
| MgO | 16·5 | .... | 330·0 | .... | 12·85 | .... | 13·61 |
| FeO | 14 | .... | 492·8 | .... | 19·19 | .... | 18·75 |
| MnO | | .... | | .... | | .... | 1·15 |
| $SiO^2$ | 42 | .... | 1302·0 | .... | 50·71 | .... | 48·83 |
| $Al^2O^3$ | 3·5 | .... | 180·1 | .... | 7·01 | .... | 7·48 |
| F—O | 1 | .... | 10·7 | .... | 0·42 | .... | 0·41 |
| HO | | .... | | .... | | .... | 0·50 |
| | | | 2567·6 | .... | 100·00 | .... | 100·89 |

| | At. | | *Uralite.* | | | | Kudernatsch. *d.* |
|---|---|---|---|---|---|---|---|
| CaO | 5 | .... | 140·0 | .... | 12·70 | .... | 12·47 |
| MgO | 7 | .... | 140·0 | .... | 12·70 | .... | 12·90 |
| FeO | 5 | .... | 176·0 | .... | 15·96 | .... | 16·37 |
| MnO | | .... | | .... | | .... | |
| $SiO^2$ | 19·2 | .... | 595·2 | .... | 53·98 | .... | 53·05 |
| $Al^2O^3$ | 1 | .... | 51·4 | .... | 4·66 | .... | 4·56 |
| | | | 1102·6 | .... | 100·00 | .... | 99·35 |

| | At. | | *Common Hornblende.* | | | | Hisinger. *e.* |
|---|---|---|---|---|---|---|---|
| CaO | 2 | .... | 56·0 | .... | 14·41 | .... | 13·92 |
| MgO | 3 | .... | 60·0 | .... | 15·44 | .... | 16·34 |
| FeO | 1 | .... | 35·2 | .... | 9·05 | .... | 7·74 |
| MnO | | .... | | .... | | .... | 1·50 |
| $SiO^2$ | 6 | .... | 186·0 | .... | 47·86 | .... | 45·38 |
| $Al^2O^3$ | 1 | .... | 51·4 | .... | 13·24 | .... | 13·82 |
| HO | | .... | | .... | | .... | 0·24 |
| | | | 388·6 | .... | 100·00 | .... | 98·94 |

*a* is the so-called Grammatite from Acre;—*b*, Hornblende from Pargas;—*c*, Hornblende from Nordmark;—*d*, Uralite from the Baltic Sea; *e*, Hornblende from Lindbo.—In *a*, the number of atoms of the stronger bases amounts to $5+12+1=18$; that of the alumina and hydrofluoric acid to $3+1=4$; and if 4 atoms of the bases are in combination with these, there remain $18-4=14$; these 14 atoms of base are to the 16·2 atoms of silicic acid in the proportion of 5 : 6. Similarly, with the other calculations.

*Ordinary Asbestos, Amianth, Wood-asbestos, Petrified Cork, Byssolite,* &c. consist of tremolite, actynolite, anthophyllite, or common hornblende in a very fine, fibrous state.

| | At. | | *Asbestos.* | | | Bonsdorff. *a.* | | Hess. *b.* | | Heintze. *c.* |
|---|---|---|---|---|---|---|---|---|---|---|
| CaO | 8·5 | .... | 238·0 | 15·34 | .... | 15·55 | .... | 0·04 | .... | |
| MgO | 16 | .... | 320·0 | 20·63 | .... | 22·10 | .... | 31·38 | .... | 31·02 |
| FeO | 1·5 | .... | 52·8 | 3·40 | .... | 3·08 | .... | 9·22 | .... | 8·27 |
| MnO | | .... | | | .... | 0·21 | .... | trace. | .... | |
| $SiO^2$ | 30 | .... | 930·0 | 59·94 | .... | 58·20 | .... | 58·48 | .... | 59·23 |
| $Al^2O^3$ | | .... | | | .... | 0·14 | .... | 0·88 | .... | 0·19 |
| F—O | 1 | .... | 10·7 | 0·69 | .... | 0·66 | | | | |
| HO | | .... | | | .... | 0·14 | .... | | .... | 1·31 |
| | | | 1551·5 | 100·00 | .... | 100·08 | .... | 100·00 | .... | 100·02 |

*a* is Asbestos from the Tarentaise;—*b*, Asbestos from Koruk, very difficult of fusion;—*c*, Asbestos from Tschussowaja in the Ural. *a* resembles

tremolite in composition, *b* and *c* resemble anthophyllite; *b* and *c* are composed of about $5FeO, 30MgO, 42SiO^2$; the quantity of silica given by the analyses is, however, rather too small for this calculation.

G. Rose (*Pogg.* 22, 321) considers that augite and hornblende belong to the same class, and for the following reasons: the angles of either of these minerals may be reduced to those of the other; crystals are found in the form of augite and with the cleavage-planes of hornblende; when crystals of augite and hornblende have grown together, their axes are parallel; the specific gravity and composition of the two minerals are identical; if the fused mass is rapidly cooled, it assumes the appearance of augite, and if slowly cooled, it seems to crystallize in the form of hornblende. When, therefore, both are found together, the hornblende surrounds the crystals of augite, which are the first produced. From this cause, hornblende is accompanied by quartz, felspar, albite, and other minerals, which are formed by the slow cooling of molten masses; augite, on the contrary, is found with olivine, which crystallizes by rapid cooling. For the same reason, slags, from being too quickly cooled, yield only crystals of augite. According to Mitscherlich and Berthier, also, the fusing together of lime, magnesia, and silica yields white crystals of augite, but none of hornblende; and even tremolite, fused by Mitscherlich and Berthier in a charcoal crucible,—or actynolite, by G. Rose, in a platinum crucible in a potter's furnace—solidified to a mass consisting of distinct crystals of augite. (G. Rose.)—It is remarkable that hornblende is always richer in silica than augite.

*d. Sesquisilicate of Magnesia and Lime.*—One atom of lime, one atom of magnesia, and 3 atoms of silica exposed to the heat of a forge, yield a very fusible enamel of the colour of pearl. (Sefström.)

## Silicium and Cerium.

Disilicate of Cerous Oxide.—*Cerite.*—Dense; specific gravity, 4·8...4·93; fracture splintered; harder than apatite; colour, dark peach-red, inclining to brown; slightly translucent at the edges. The mineral yields water when heated; it is infusible before the blowpipe alone, but dissolves slowly in borax in the inner flame, forming a dark yellow glass, which becomes colourless as it cools; but by *flaming*, or exposure to interrupted blasts, it is rendered enamel-white; it behaves in a similar manner with microcosmic salt, excepting that, in this case, an infusible skeleton of silica remains; with carbonate of soda it yields a dark yellow slag. Cerite in a finely-divided state dissolves easily in hydrochloric acid (and still more easily after ignition), with separation of gelatinous silica.

| | *Cerite.* | | Hisinger. | Vauquelin. |
|---|---|---|---|---|
| $2CeO$ | 108 | 68·78 | 68·59 | 67 |
| $SiO^2$ | 31 | 19·75 | 18·00 | 17 |
| $2HO$ | 18 | 11·47 | 9·60 | 12 |
| $CaO$ | | | 2·00 | 2 |
| $Fe^2O^3$ | | | 1·25 | 2 |
| $2CeO, SiO^2 + 2Aq.$ | 157 | 100·00 | 99·44 | 100 |

With the protoxide of cerium, oxide of lanthanum and oxide of didymium are also mixed (Mosander); cerite likewise contains traces of yttria and cobalt. (Berzelius.)

## Silicium and Yttrium.

A. Silicate of Yttria.—*Gadolinite*, or *Ytterite*.—Amorphous; specific gravity 4·0 to 4·35. Harder than felspar. Black, passing into a greenish or brownish colour; translucent at the edges; greyish green when in a state of powder.

*a. Trisilicate*—3YO, $SiO^2$.—*Splintery Gadolinite*.—Of a splintery fracture. When heated, it sometimes, though rarely, emits a faint light; the principal varieties evolve a small portion of water, and swell up to a cauliflower-like mass. In borax it dissolves readily; but in microcosmic salt with great difficulty and not completely: the glass has a green colour, arising from the presence of protoxide of iron. With a small quantity of carbonate of soda, it forms a fused globule; but with a larger proportion, a reddish brown, semi-vitrefied slag. The gadolinite of Kararfvet, when heated, yields but a small quantity of water; becomes white without swelling up, and fuses to a grey or reddish-coloured, turbid glass; it dissolves readily in borax, forming a glass which is slightly coloured by iron, and, when saturated with gadolinite, appears turbid and crystallizes on cooling to a grey mass. Microcosmic salt dissolves it, with separation of a skeleton of silica, forming a nearly colourless glass, which becomes opalescent as it cools: the mineral fuses with difficulty in carbonate of soda, forming a greyish red slag. (Berzelius.)—Splintery gadolinite dissolves in hydrochloric acid with separation of gelatinous silica, but not after ignition.

| | At. | | *Splintery Gadolinite.* | | | Scheerer. *a.* |
|---|---|---|---|---|---|---|
| CaO | | .... | | | .... | 0·23 |
| CeO | | .... | | | .... | |
| LaO | 2 | .... | 88·0 | 5·99 | .... | 6·33 |
| YO | 17 | .... | 680·0 | 46·31 | .... | 44·96 |
| GO | 12 | .... | 152·4 | 10·38 | .... | 10·18 |
| FeO | 5 | .... | 176·0 | 11·99 | .... | 12·13 |
| $SiO^2$ | 12 | .... | 372·0 | 25·33 | .... | 25·59 |
| HO | | .... | | | .... | |
| | | | 1468·4 | 100·00 | .... | 99·42 |

| | Berzelius. | | | | |
|---|---|---|---|---|---|
| | *b.* | | *c.* | | *d.* |
| CaO | | .... | | .... | 3·15 |
| CeO | 16·69 | .... | 16·90 | $Ce^2O^3$ | 3·40 |
| LaO | | .... | | $Mn^2O^3$ | 1·30 |
| YO | 45·00 | .... | 45·93 | .... | 47·30 |
| GO | | .... | | .... | 2·00 |
| FeO | 10·26 | .... | 11·34 | $Fe^2O^3$ | 8·00 |
| $SiO^2$ | 25·80 | .... | 24·16 | .... | 29·18 |
| HO | 0·60 | .... | 0·60 | .... | 5·20 |
| | 98·35 | .... | 98·93 | .... | 99·53 |

*a*, is Gadolinite from Hitterön;—*b*, from Finbo;—*c*, from Broddbo;—*d*, from Kararfvet;—The calculation is made from *a*; in the other analyses, the oxide of lanthanum, a base unknown at the time when they were made, was not taken into account. In all varieties of gadolinite, a portion of the yttria is replaced by several other bases.

*b. Disilicate of Yttria.—Vitreous Gadolinite.*—Of conchoidal fracture. When gradually heated, it emits a bright phosphorescent light (I., 107) of

a greyish green colour; at the same time it increases slightly in density, and swells up a little; before the blowpipe it turns black at the edges, but does not fuse. Its behaviour with borax, microcosmic salt, carbonate of soda, and hydrochloric acid, is similar to that of *a*.

| | At. | *Conchoidal Gadolinite.* | | Berlin, of Ytterby. *a.* | *b.* |
|---|---|---|---|---|---|
| KO | .... | | .... | 0·19 | 0·21 |
| NaO | .... | | .... | 0·18 | 0·20 |
| CaO | .... | | .... | 1·30 | 0·50 |
| MgO | .... | | .... | 0·54 | 0·11 |
| CeO | 3 | 162·0 | 8·55 .... | 7·90 | 6·08 |
| YO | 24 | 960·0 | 50·65 .... | 50·00 | 45·53 |
| FeO | 7 | 246·4 | 13·00 .... | 14·44 | 20·28 |
| $SiO^2$ | 17 | 527·0 | 27·80 .... | 25·62 | 25·26 |
| $Al^2O^3$ | .... | | .... | 0·48 | 0·28 |
| | | 1895·4 | 100·00 .... | 100·65 | 98·45 |

B. Fluoride of Silicium and Yttrium.—Insoluble in pure water, but dissolved by water containing hydrochloric acid; on the evaporation of the liquid, it separates again.

## Silicium and Glucinum.

A. Silicate of Glucina.—*Phenakite.*—Primary form, a truncated rhombohedron, *Fig.* 141; ordinary form, *Fig.* 145, with the lateral edges and lateral solid angles replaced by secondary faces; $r^3 : r^3 = 115° 25'$ (116° 40' Beirich); $r^1 : r^3$ or $r^5 = 65° 35'$; $r : \rho = 147° 42\frac{1}{2}'$. Cleavage parallel to the faces which replace the lateral edges (or to the faces of the six-sided prism.) The mineral is harder than quartz, but softer than topaz; has the fracture of quartz; specific gravity = 2·969 (3·0 Beirich.) Transparent and colourless, with a glassy lustre, and often yellowish. Infusible before the blowpipe. Dissolves in borax, forming a clear glass, from which, when saturated, opaque flakes are separated by flaming; in microcosmic salt, it dissolves very slowly (leaving at the same time a skeleton of silica) and forms a bead which, if saturated, becomes enamel-like on cooling. With carbonate of soda, in any proportions, it does not give a clear glass but only a white enamel.

Ignited with solution of cobalt, it assumes a dirty bluish colour: (Nordenskiold, *Pogg.* 31, 67.)

| | *Phenakite.* | | Hartwall. Perm. | Beirich. Framont. | Rose. Ilmengebirge. |
|---|---|---|---|---|---|
| 2GO | 25·4 | 45·63 .... | 44·47 .... | 45·54 .... | 15·08 |
| $SiO^2$ | 31·0 | 54·97 .... | 55·14 .... | 54·37 .... | 65·45 |
| Magnesia and Sesquioxide of Iron | | .... | traces .... | 0·09 ($Al^2O^3$ + trace of $Fe^2O^3$) | 19·48 |
| 2GO, $SiO^2$ .... | 56·4 | 100·00 .... | 99·61 .... | 100·00 .... | 100·01 |

B. Fluoride of Silicium and Glucinum.—The aqueous solution yields on evaporation a clear syrupy liquid, which finally becomes opaque and white; if the salt was dissolved in an excess of acid, it remains, after the volatilization of the latter, in hard, white masses, resembling porcelain. The salt has a rough taste without any degree of sweetness. When heated till decomposition commences, it swells up slightly. It dissolves readily in water. (Berzelius.)

C. Silicate of Glucina and Lime.—*Leucophane* is a compound of this double salt with fluoride of sodium. Cleavage parallel to the faces of a rhombic prism; specific gravity = 2·974; pale green or yellow, with a glassy lustre. Fuses before the blowpipe to a transparent, violet-coloured bead, which becomes opaque by flaming. It dissolves easily and in large quantity in borax, yielding an amethyst-coloured glass,—in microcosmic salt, with evolution of gaseous fluoride of silicium and separation of an insoluble skeleton of silica;—with carbonate of soda, it yields a turbid bead which does not sink into the charcoal. (Erdmann, *Jahresbericht*, 21, 2,168.)

| | At. | | *Leucophane.* | | | Erdmann. |
|---|---|---|---|---|---|---|
| CaO | 3 | .... | 84·0 | 26·34 | .... | 25·00 |
| MnO | | .... | | | .... | 1·01 |
| GO | 3 | .... | 38·1 | 11·94 | .... | 11·51 |
| $SiO^2$ | 5 | .... | 155·0 | 48·59 | .... | 47·82 |
| K | | .... | | | .... | 0·26 |
| Na | 1 | .... | 23·2 | 7·27 | .... | 7·59 |
| F | 1 | .... | 18·7 | 5·86 | .... | 6·17 |
| | | | 319·0 | 100·00 | .... | 99·36 |

$3(CaO, SiO) + 3GO, 2SiO^2 + NaF.$

## Silicium and Aluminum.

A. Silicate of Alumina.—*a. Disilicate of Alumina.—Hydrated.—α. Collyrite.*—Very soft, earthy, and unctuous to the touch, adhering strongly to the tongue. In water it becomes transparent, and crumbles to pieces; it dissolves in acids, and the solution yields a jelly on evaporation.—*β. Opaline Allophane.*—Specific gravity, 1·985 to 2·015; with conchoidal fracture and glassy lustre; colour, greenish white. When heated it evolves water with slight decrepitation; swells up before the blowpipe without fusing; with microcosmic salt it forms a transparent bead. It dissolves in warm dilute hydrochloric acid with separation of gelatinous silica. (Schrötter.)

| | *Collyrite.* | | Klaproth. *a.* | Berthier. *b.* | Schrötter. *c.* |
|---|---|---|---|---|---|
| $2Al^2O^3$ | 102·8 | 45·94 | .... 45 | .... 44·5 | .... 46·30 |
| $SiO^2$ | 31·0 | 13·85 | .... 14 | .... 15·0 | .... 11·95 |
| 10HO | 90·0 | 40·21 | .... 42 | .... 40·5 | .... 35·85 |
| CaO, 1·16; CuO, 0·25; $F^2O^3$, 2·80; $SO^3$, 0·63; total | | | .... | .... | .... 4·84 |
| $2Al^2O^3, SiO^2 + 10Aq.$ | 223·8 | 100·00 | .... 101 | .... 100·0 | .... 98·94 |

*a* is Collyrite from Schemnitz;—*b*, from Esquerra;—*c*, is Opaline Allophane from Steiermark.

*b. Two-thirds Silicate of Alumina.*—This is probably the composition of *Staurolite*, excepting that about one-third of the alumina is replaced by sequioxide of iron. This mineral belongs to the right prismatic system of crystallization. *Fig.* 61, 68, without the *i*-face, and *Fig.* 70; $p : u = 93°$; $u^1 : u = 129° 30'$; $u : t = 115° 15'$; $u : y = 137° 37'$; $p : y = 125° 16'$. Cleavage parallel to *p*, *u*, and *t*. (Hauy.) The crystals frequently intersect each other in the shape of a cross at angles of 90° or 120°. Specific gravity, from 3·5 to 3·8. Harder than quartz. Translucent; dark-red or brown. When in the state of fine powder, it fuses

before the blowpipe to a black slag at the edges. It dissolves slowly in borax, forming a clear, dark-green glass; when reduced to powder, it dissolves with difficulty, but almost entirely in microcosmic salt, yielding a bead which is transparent and greenish yellow while hot, but becomes colourless and opaque on cooling. With carbonate of soda, it effervesces and yields a yellow slag. (Berzelius.) Hydrochloric acid does not act on staurolite; sulphuric acid decomposes it partially, either before or after ignition. (Von Kobell.)

| | At. | | *Staurolite.* | |
|---|---|---|---|---|
| $Fe^2O^3$ | 1 | .... | 35·2 | 17·6 |
| $MnO^3$ | | .... | | |
| $Al^2O^3$ | 2 | .... | 102·8 | 51·4 |
| $SiO^2$ | 2 | .... | 62·0 | 31·0 |
| MgO | | .... | | |
| $2Al^2O^3, Fe^2O^3 + 2SiO^2$ | 1 | .... | 200·0 | 100·0 |

| | Klaproth. | | | | Vauquelin. | | Descotils. |
|---|---|---|---|---|---|---|---|
| | *a.* | | *b.* | | *c.* | | *d.* |
| $Fe^2O^3$ | 18·50 | .... | 18·25 | .... | 13·00 | .... | 9·5 |
| $MnO^3$ | 0·25 | .... | 0·50 | .... | 1·00 | | |
| $Al^2O^3$ | 52·25 | .... | 41·00 | .... | 44·00 | .... | 40·0 |
| $SiO^2$ | 27·00 | .... | 37·50 | .... | 33·00 | .... | 48·0 |
| MgO | | .... | 0·50 | CaO | 3·84 | | |
| | 98·00 | .... | 97·75 | .... | 94·84 | .... | 97·5 |

*a* is reddish brown—*b*, blackish brown Staurolite, from Gotthard;—*c* and *d* are from Brittany. With such inadequate results of analysis, the calculation given must be regarded as merely hypothetical.

*c. Monosilicate of Alumina.*—*α. Anhydrous.* $Al^2O^3, SiO^2$.—The following minerals appear to possess this composition. 1. *Andalusite* and *Chiastolite.*—Right rhombic prisms, with angles of 91° 35′ and 88° 27′; cleavage parallel to *u*, *m*, and *t*. Specific gravity of Andalusite, from 3·0 to 3·2; of Chiastolite from 2·94 to 3·09.—Harder than quartz (Chiastolite is softer than felspar.) Infusible. Dissolves with difficulty in borax, forming a clear glass, and with still greater difficulty and less perfectly in microcosmic salt. Ignited in powder with solution of cobalt, it assumes a blue colour. Insoluble in acids.

| | At. | | *Andalusite.* | | Bucholz. *a.* | | Bunsen. *b.* | | *Chiastolite*, c. |
|---|---|---|---|---|---|---|---|---|---|
| $Al^2O^3$ | 1 | .... | 51·4 | 62·38 | 60·5 | .... | 58·62 | .... | 58·56 |
| $SiO^2$ | 1 | .... | 31·0 | 37·62 | 36·5 | .... | 40·17 | .... | 39·09 |
| $Fe^2O^3$ | | .... | | .... | 4·0 | | | | |
| $Mn^3O^4$ | | .... | | .... | | .... | 0·51 | .... | 0·53 |
| CaO | | .... | | .... | | .... | 0·28 | .... | 0·21 |
| HO | | .... | | .... | | .... | | .... | 0·99 |
| | 1 | .... | 82·4 | 100·00 | 101·0 | .... | 99·58 | .... | 99·38 |

*a* is Andalusite from Herzogau;—*b*, from Lisens;—*c* is Chiastolite from Lancaster. The calculation gives more alumina than the analyses; in the latter, however, lime, sesquioxide of iron, and sequioxide of manganese are found; and part of the silica is in combination with them.

2. *Cyanite.*—Crystalline system, the doubly-oblique prismatic; *Fig.* 121, with the faces *w*, *n*, and others; $y : u = 108° 55'$; $y : v = 94° 38'$; $u : v = 106° 6'$. Cleavage parallel to *v*; less distinct, parallel to *u*; and *still less distinct*, parallel to *y*. (Hauy.) Specific gravity, from 3·54 to 3·67.

On the *v*-faces harder, on the *u*-faces softer than felspar. Transparent and of a pearly lustre on the *v* faces; generally blue. Before the blowpipe it does not fuse but becomes colourless; it dissolves with difficulty, but nevertheless completely, in borax, forming a transparent glass; and also in phosphate of soda, with the exception of a blistered, translucent skeleton of silica; with a small quantity of carbonate of soda, it fuses imperfectly to a rounded, blistered, translucent mass, which, in the outer blowpipe flame, generally assumes a rose colour; when strongly ignited with solution of cobalt, it becomes dark blue. (Berzelius.) Acids do not attack cyanite.

| | | | Cyanite. | | Rosales. | Arfvedson. | |
|---|---|---|---|---|---|---|---|
| | At. | | | | *a.* | *b.* | *c.* |
| $Al^2O^3$ | 1 | 51·4 | 62·38 | | 63·11 | 64·89 | 63·8 |
| $SiO^2$ | 1 | 31·0 | 37·62 | | 36·67 | 34·33 | 36·4 |
| KO | | | | | | | |
| CaO | | | | | | | |
| $Fe^2O^3$ | | | | | 1·19 | | |
| | 1 | 82·4 | 100·00 | | 100·97 | 99·22 | 100·2 |

| | Beudant. | Chenevix. | Connell. |
|---|---|---|---|
| | *d.* | *e.* | *f.* |
| $Al^2O^3$ | 67·8 | 58·00 | 58·94 |
| $SiO^2$ | 31·6 | 38·00 | 36·75 |
| KO | 0·2 | | |
| CaO | 0·2 | | |
| $Fe^2O^3$ | | 0·75 | 0·99 |
| | 99·8 | 96·75 | 96·68 |

*a* and *b* are Cyanite from St. Gotthard;—*c*, from Röraas;—*d*, from Zillerthal;—*e* is *Fibrolite* from the East:—*f*, *Sillimanite*.

The *Talc-lithomarge* of Rochlitz, according to the analysis of Kerstens (*Schw.* 66, 16), is likewise composed of $Al^2O^3$, $SiO^2$.

*β. Hydrated Monosilicate of Alumina.*—Soft, amorphous masses, which give up water when heated, but do not fuse.—1. *Miloschine.*—Specific gravity = 2·031; translucent at the edges. In water it decrepitates and falls to pieces. Dissolves but partially in hydrochloric acid. (Kersten.)

2. The so-called *Collyrite* of Weissenfels; unctuous to the touch; adhering strongly to the lips; opaque. It dissolves in hydrochloric acid, the whole of the silica being separated in the gelatinous form. (Kersten.)

3. *Allophane.*—Specific gravity, 1·76 to 1·89;—fracture, flatly conchoidal, passing into the plane. Adheres to the tongue. Transparent; pale greenish blue or yellowish white. By ignition it becomes white, opaque, and full of fissures. It dissolves perfectly in dilute acids; when digested in concentrated acids, it leaves a siliceous jelly.

| | At. | *Miloschine.* | | Kersten. |
|---|---|---|---|---|
| $Al^2O^3$ | 1 | 51·4 | 46·98 | 45·01 |
| $SiO^2$ | 1 | 31·0 | 28·34 | 27·50 |
| HO | 3 | 27·0 | 24·68 | 23·30 |
| CaO | | | | 0·30 |
| MgO | | | | 0·20 |
| $Cr^2O^3$ | | | | 3·61 |
| | 1 | 109·4 | 100·00 | 99·92 |

| | At. | *Allophane.* | | Kersten. *a.* | Guillemin. *b.* | Wakinar. *c.* |
|---|---|---|---|---|---|---|
| $Al^2O^3$ | 1 | 51·4 | 40·35 | 42·8 | 39·68 | 38·76 |
| $SiO^2$ | 1 | 31·0 | 24·34 | 23·3 | 23·76 | 24·12 |
| HO | 5 | 45·0 | 35·31 | 33·7 | 35·74 | 35·75 |
| CaO | | | | | trace. | 2·53 |
| MgO | | | | | | |
| $Cr^2O^3$ | | | | | $SO^3$ 0·65 | |
| | 1 | 127·4 | 100·00 | 99·8 | 99·83 | 100·96 |

| | *Allophane.* | | Bunsen. *d.* | Guillemin. *e.* | Stromeyer. *f.* | Berthier. *g.* |
|---|---|---|---|---|---|---|
| $Al^2O^3$ | 51·4 | 35·35 | 32·18 | 35·00 | 32·20 | 29·2 |
| $SiO^2$ | 31·0 | 21·32 | 22·30 | 22·00 | 21·92 | 21·9 |
| 7HO | 63·0 | 43·33 | 42·62 | 42·00 | 41·30 | 44·2 |
| $Fe^2O^3$ | | | 2·90 | | 0·27 | |
| $SO^3$ | | | | 0·75 | | Clay 4·7 |
| CaO 0·73; $CaO,SO^3$ 0·52; $CaO,SO^3$ 3·06: total | | | | | 4·31 | |
| | 145·4 | 100·00 | 100·00 | 99·75 | 100·00 | 100·0 |

*a* is the so-called Collyrite from Weissenfels;—*b*, Allophane from Firmi, dried at 100°;—*c*, Allophane from Gersbach;—*d*, Allophane from Friesdorf; *e*, Allophane from Firmi, dried in the air; *f*, Allophane from Gräfenthal;—*g*, Allophane from Beauvais. As the allophane of Firmi, which retains 7 atoms of water when dried in the air, loses 2 atoms at 100°—these 2 atoms being doubtless attached to it merely as hygroscopic water—it may be concluded that the other varieties of allophane after being exposed to a temperature of 100°, do not contain more than 5 atoms of water. The *Bole of Sinope*, according to the analysis of Klaproth, is nearly $(Fe^2O^3, Al^2O^3)\,SiO^3 + 2Aq$.

*d. Sesquisilicate of Alumina.*—*α. Anhydrous.*—*Bucholzite* and *Xenolite*, unless these minerals are merely fibrous varieties of cyanite. Xenolite is fibrous, of specific gravity 3·58, and as hard as quartz. (Nordenskiold, *Pogg.* 56, 643.)

| | At. | | | Brandes. *a.* | Thomson. *b.* | Komonen. *c.* |
|---|---|---|---|---|---|---|
| $Al^2O^3$ | 2 | 102·8 | 52·5 | 50·0 | 52·92 | 52·54 |
| $SiO^2$ | 3 | 93·0 | 47·5 | 46·0 | 46·40 | 47·44 |
| $Fe^2O^3$ | | | | 2·5 | | |
| KO | | | | 1·5 | | trace. |
| $2Al^2O^3, 3SiO^2$ | 1 | 195·8 | 100·0 | 100·0 | 99·32 | 99·98 |

*a* is Bucholzite from Faltigl;—*b*, from Chester on the Delaware;—*c* is Xenolite from Finland.

Sefström did not succeed in fusing a mixture of 2 atoms of alumina with 3 atoms of silica in the most powerful blast-furnace.

*β. Hydrated.*—1. The *Wörthite* of Hess (*Pogg.* 21, 73) appears to be: $2Al^2O^3, 3SiO^2 + Aq.$; but there is a deficiency of silica.—2. *Pholerite.*—Soft; adheres to the tongue; produces a doughy mass with water; of a pearly lustre; white; insoluble in nitric acid. (Guillemin.)

| | | | Guillemin. |
|---|---|---|---|
| $2Al^2O^3$ | 102·8 | 44·35 | 43·89 |
| $3SiO^2$ | 93·0 | 40·12 | 40·75 |
| 4HO | 36·0 | 15·53 | 15·36 |
| $2Al^2O^3, 3SiO^2 + 4Aq.$ | 231·8 | 100·00 | 100·00 |

e. *Bisilicate of Alumina.*—*α. Anhydrous.*—Pure burnt clay.

*β. Hydrated.*—*Clay.*—Nearly all pure clay consists of $Al^2O^3, 2SiO^2 + 2Aq$. In nature, however, it is generally found mixed with carbonate of lime, magnesia, and protoxide of iron, from which it acquires the property of effervescing with acids; also with hydrated sesquioxide of iron and hydrated sesquioxide of manganese, finely divided quartz, felspar, albite, mica, spodumene, organic matter, &c., all of which modify its properties and applications to a considerable extent. The presence of potash, lime, sesquioxide of iron, &c., renders it more fusible. From the coarser impurities it may be separated by elutriation.

Clay is produced by the decomposition of felspar, albite, and similar compounds, from which the silicate of potash is dissolved out by water. Pure clay is soft, more or less unctuous to the touch, white and opaque, and emits a characteristic odour when breathed upon. Bouis (*J. Pharm.* 13, 282) attributes this odour to the ammonia contained in the clay, in so far as the ammonia may serve as the vehicle of the odour. Accordingly, clay emits a stronger smell when treated with solution of caustic potash, by which the ammonia is expelled; but after the ammonia is all driven off, the odour ceases entirely. Clay is converted by water into a doughy mass, of various degrees of tenacity, but loses this quality on drying. When rapidly heated, it cracks in every direction; but when slowly heated, it parts with its water at a temperature below redness, and at the same time decreases in bulk; if heated to redness, it still continues porous, and may be saturated with water, but it no longer falls to pieces when put into water. The stronger the heat to which it is exposed, the more dense, sonorous, and hard does the clay become. At a very high temperature the pores contract, but the specific gravity of the clay, taken in a state of powder, increases only up to a dull red heat; at a higher temperature, it again diminishes. Kaolin dried at 100° has a specific gravity of 2·47; after drying at 150° (302° F.), of 2·53; at 300° (572° F.) of 2·60; after ignition at a low red heat, of 2·70; at a strong red heat, 2·64; at incipient whiteness, 2·50; and after exposure to a full white heat, the specific gravity falls to 2·48. (Laurent, *Ann. Chim. Phys.* 66, 96.) Pure clay does not fuse in the most powerful blast-furnaces; it becomes, however, soft enough to be bent for pipe-stems. Clay dissolves with difficulty in borax, forming a transparent glass; with phosphate of soda it forms a glass which is transparent and white while hot, and becomes opalescent as it cools, a skeleton of silica being also separated; with carbonate of soda, it forms a green glass, if iron is also present; ignited with solution of cobalt, it generally assumes a blue colour. Clay does not dissolve in dilute hydrochloric or nitric acid; but diluted oil of vitriol boiled with the clay till the acid itself begins to evaporate, dissolves out the alumina together with a small quantity of silica, and separates the greater portion of the silica, in the more soluble condition in which it dissolves in a boiling solution of carbonate of soda: the quartz-sand, felspar, &c., frequently mixed with the clay, remain behind. (Forchhammer.) By boiling clay with a solution of potash, a double silicate of alumina and potash is formed, which is dissolved more perfectly in proportion to the excess of potash employed. Clay carefully heated till the whole of the water is expelled, still remains soluble in sulphuric acid and potash; by ignition, however, its solubility is destroyed. One part of kaolin fused with 3 parts of hydrate of potash, yields a pasty mass; and with from 5 to 10 parts, a very fluid mass. From this mass, water dissolves out potash, together with alumina and silica, the quantity increasing as

the potash predominates; the residue consists of a double silicate of alumina and potash. One part of kaolin heated to redness with 5 parts of dry carbonate of soda does not fuse, and yields scarcely anything but pure soda when treated with water. After exposure to a white heat, however, the same results are obtained as with hydrate of potash. (Berthier.)

| | At. | | | | |
|---|---|---|---|---|---|
| $Al^2O^3$ ..... | 1 | .... | 51·4 | .... | 39·12 |
| $SiO^2$ ..... | 2 | .... | 62·0 | .... | 47·19 |
| HO ..... | 2 | .... | 18·0 | .... | 13·69 |
| | 1 | .... | 131·4 | .... | 100·00 |

| | Forchhammer. | | | | | |
|---|---|---|---|---|---|---|
| | *a.* | *b.* | *c.* | *d.* | *e.* | *f.* |
| $Al^2O^3$ ..... | 37·71 | 39·60 | 38·34 | 39·13 | 38·24 | 35·81 |
| $SiO^2$ ..... | 48·17 | 46·68 | 48·71 | 46·62 | 47·26 | 50·99 |
| HO ..... | 14·12 | 13·72 | 12·95 | 14·25 | 14·50 | 13·20 |
| | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |
| Soluble ..... | 23·67 | 3·24 | 4·10 | 4·27 | 2·25 | 13·75 |
| Insoluble .... | 47·87 | 5·39 | 68·29 | 4·19 | 2·48 | 205·17 |
| | 171·54 | 108·63 | 172·29 | 108·46 | 104·73 | 318·92 |

| | Forchhammer. | | Berthier. | | | Boase. | |
|---|---|---|---|---|---|---|---|
| | *g.* | *h.* | *i.* | *k.* | *l.* | *m.* | *n.* |
| $Al^2O^3$ ..... | 37·39 | 40·87 | 37·88 | 41·25 | 40·13 | 41·14 | 42·23 |
| $SiO^2$ ..... | 49·30 | 44·42 | 47·66 | 46·25 | 47·52 | 45·62 | 43·90 |
| HO ..... | 13·31 | 14·71 | 14·46 | 12·50 | 12·35 | 13·24 | 13·87 |
| | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |
| Soluble .... | 1·31 | 2·94 | 0·82 | | 1·27 | 1·99 | 1·61 |
| Insoluble.... | 93·60 | 19·61 | | 25·00 | 4·33 | 10·80 | 9·66 |
| | 194·91 | 122·55 | 100·82 | 125·00 | 105·60 | 112·79 | 111·27 |

The specimens of clay examined by Forchhammer were dried at 100° before analysis, and then heated with sulphuric acid to obtain the results; Berthier treated them alternately with a boiling solution of caustic potash and hydrochloric acid. The insoluble residue remaining after these processes, and consisting chiefly of quartz-sand and felspar, is designated by *Insol.*; the foreign substances in the clay which passed over with the solution, by *Sol.* For the sake of clearness, the pure clay is calculated to 100 parts; for instance in *a*, the 171·54 parts of the clay experimented on contain 100 parts of pure clay, 23·67 parts of soluble and 47·87 parts of insoluble foreign matters.

a. *Porcelain clay* of Sedlitz. *Sol.* Carbonate of lime and an undetermined substance, with traces of potash and soda; *Insol.* Quartz-sand.

b. *Porcelain clay* from Schneeberg. *Sol.* Carbonate of lime with a trace of soda.

c. *Porcelain clay* from Halle. *Sol.* Potash, carbonate of lime, magnesia, sesquioxide of manganese, and sesquioxide of iron.

d. *Porcelain clay* from Bornholm. *Sol.* Potash, carbonate of lime, magnesia, sesquioxide of manganese, and sesquioxide of iron.

e. *Earthy Lenzinite* from Kall. *Sol.* The sesquioxides of manganese and iron, with traces of potash and carbonate of lime.

f. *Elutriated Clay* from Grossalmerode. *Sol.* Potash, the sesquioxides of manganese and iron, and a trace of carbonate of lime.

g. *Porcelain clay* from Limoges. *Sol.* Soda, magnesia, and sesquioxide of manganese.

h. Another specimen of the same. *Sol.* Magnesia; *Insol.* Felspar containing potash and magnesia.

i. *White clay* from Siegen. The soluble part consists of magnesia.

k. *Washed Porcelain clay* from Turascon. *Insol.* Quartz, and apparently, soda-spodumene.

l. *Washed Porcelain clay* from Pamiers. *Sol.* Lime and magnesia. *Insol.* Quartz and soda-spodumene.

m and n. *Best Porcelain clay* from Breage and St. Stephen's in Cornwall. *Sol.* Magnesia; *Insol.* Quartz and talc.

[On this subject, see more particularly Forchhammer, *Pogg.* 35, 331; Berthier, *Ann. Chim. Phys.* 62, 225; also *J. pr. Chem.* 10, 28.]

The *Porcelain clay of Passau* differs from the preceding by containing one atom more of water.

| | | | | Fuchs. | | Forchhammer. |
|---|---|---|---|---|---|---|
| $Al^2O^3$ | 51·4 | 36·61 | .... | 36·63 | .... | 35·97 |
| $2SiO^2$ | 62·0 | 44·16 | .... | 44·51 | .... | 46·39 |
| 3HO | 27·0 | 19·23 | .... | 18·86 | .... | 17·64 |
| $Al^2O^3, 2SiO^2 + 3Aq$ | 140·4 | 100·00 | .... | 100·00 | .... | 100·00 |
| Carbonate of lime | | | | 0·90 | .... | 3·02 |
| Magnesia, sesquioxides of iron and manganese | | | | | | |
| Insoluble matter | | | | 1·02 | .... | 3·73 |
| | | | | 101·92 | .... | 106·75 |

Many *hardened varieties of Lithomarge* (*Steinmark*) have nearly the same composition as clay:

| | Klaproth. *a.* | | Zellner. *b.* |
|---|---|---|---|
| $Al^2O^3$ | 36·50 | .... | 36·2 |
| $SiO^2$ | 45·25 | .... | 49·2 |
| HO | 14·00 | .... | 14·0 |
| $Fe^2O^3$ | 2·75 | .... | 0·5 |
| KO | trace. | | |
| | 98·50 | .... | 99·9 |

*a.* Lithomarge from Rochlitz; *b*, from Buchberge near Landshut.

*Halloyte* or *Halloysite* also appears from its composition to be nothing more than ordinary clay; it is true that when dried in the air it contains a larger proportion of water, which amounts to nearly 4 atoms; but when dried in the kiln, it is found to contain not much more than clay itself. Halloyte occurs in white, soft, smooth masses, with conchoidal, waxy fracture, adhering to the tongue, opaque, or translucent at the edges only, not falling to pieces when put into water, but increasing in translucency. It is readily decomposed by oil of vitriol.

| | Berthier. | | | | Boussingault. | |
|---|---|---|---|---|---|---|
| | *a*, 1. | *a*, 2. | *b*, 1. | *b*, 2. | *c*, 1. | *c*, 2. |
| $Al^2O^3$ | 35·49 | 32·4 | 39·06 | 34·0 .... | 39·4 | 35 |
| $SiO^2$ | 47·75 | 43·6 | 44·94 | 39·5 .... | 44·9 | 40 |
| HO | 16·76 | 23·0 | 16·00 | 26·5 .... | 15·7 | 25 |
| | 100·00 | 99·0 | 100·00 | 100·0 .... | 100·0 | 100 |

| | Oswald. | | Dufrénoy. | |
|---|---|---|---|---|
| | *d.* | | *e.* | *f.* |
| $Al^2O^3$ | 35·00 | .... | 33·66 | 32·45 |
| $SiO^2$ | 40·25 | .... | 40·66 | 43·10 |
| HO | 24·25 | .... | 24·83 | 22·30 |
| MgO | 0·25 | .... | | 1·70 |
| | 99·75 | .... | 99·15 | 99·55 |

*a.* Halloyte from Housscha near Bayonne; (1) kiln-dried; (2) dried in the open air; *b*, from Angleur near Liège; (1) kiln-dried; (2) dried in the air. Both *a* and *b* were completely decomposed by cold oil of vitriol, with separation of gelatinous silica.—*c*, from Guateque in New Granada; (1) dried at 100°; (2) dried in the open air; this specimen contained a trace of chloride of ammonium;—*d*, from Upper Silesia, containing a trace of manganese;—*e*, from La Vouth;—*f*, from Thiviers.

*Bole* chiefly consists of hydrated bisilicate of alumina, in which a portion of the alumina is replaced by sesquioxide of iron. It contains, according to the manner in which it is dried, either 2 or 4 atoms of water; at least, according to the analysis of Wackenroder. (*Kastn. Arch.* 11, 466.) It is soft, with a conchoidal fracture, and of a brownish yellow colour inclining to blackish brown; translucent at the edges, or in many cases perfectly opaque;—adheres strongly to the tongue; in water it separates into small pieces with a noisy evolution of air-bubbles. Bole fuses easily to a yellow or green enamel.

*f. Tersilicate of Alumina.*—One atom of alumina heated with 3 atoms of silica in the strongest heat of the blast furnace, yields a dense, white, semi-vitrified mass. (Sefström.) The lithomarge of the Oemrichsberg consists of about : $Al^2O^3$, $3SiO^2$ + Aq.—*Razoumoffskin*, of : $Al^2O^3$, $3SiO^2$ + 3Aq.

¶ The *Salt-clay* (*salzthon*) examined by Schaf haütl appears to be a tersilicate of alumina mixed with carbonate of magnesia and other substances. It is obtained from the so-called *Haselgebirge* occurring in certain salt formations. The Haselgebirge may be separated mechanically into granular rock-salt, and a grey mass interspersed with salt, which Humboldt has named salt-clay (salzthon). Its formula, according to the following analysis, is $(Al^2O^3, 3SiO^3) + MgO, CO^2$.

| | | *Salt-clay.* | |
|---|---|---|---|
| $Al^2O^3$ | 51·4 | .... | 15·0 |
| $3SiO^3$ | 93·0 | .... | 45·5 |
| MgO | 20·0 | .... | 12·8 |
| $CO^2$ | 22·0 | .... | 13·7 |
| Fe | | .... | 6·9 |
| Mn | | .... | 0·3 |
| S | | .... | 2·2 |
| NaCl | | .... | 1·1 |
| Bitumen | | .... | 2·4 |
| | 186·4 | .... | 99·9 |

(*Ann. Pharm.* 51, 261.) ¶

*g. Quadrosilicate of Alumina.*—*α. Anhydrous.*—Under this head may probably be included Thomson's *Nacrite* (occurring in brilliant, pale-green, flexible, inelastic scales, of specific gravity 2·788), and Göbel's so-called *Tersilicate of Alumina*.

| | At. | | | | Thomson. | | Göbel. |
|---|---|---|---|---|---|---|---|
| $Al^2O^3$ ..... | 1 | .... | 51·4 | 29·3 | .... 28·84 | .... | 27·03 |
| $SiO^2$ ..... | 4 | .... | 124·0 | 70·7 | .... 64·44 | .... | 72·97 |
| FeO ..... | | .... | | | .... 4·43 | | |
| HO ..... | | .... | | | .... 1·00 | | |
| | 1 | .... | 175·4 | 100·0 | .... 98·71 | .... | 100·00 |

*β. Hydrated.*—The red *Agalmatolite* examined by Klaproth consists of about, $Al^2O^3, 4SiO^2 + Aq.$ (that analyzed by Lychnell is $Al^2O^3, 5SiO^2$; another variety is composed of silicate of magnesia; and a second, of double silicate of alumina and potash)—Klaproth's *Cimolite* and Berthier's *Kaolin of Ellnbogen* consist of $Al^2O^3, 4SiO^2 + 3Aq.$

*h. Octosilicate of Alumina.*—*Malthacite* analyzed by Meissner appears to be $Al^2O^3, 8SiO^2 + 20Aq.$

*Earthenware.*—Upon the property which clay possesses of being converted by ignition into a stony mass which no longer falls to pieces in water, depends its employment in the preparation of bricks and vessels of various kinds. To diminish its contraction in drying and burning, it is generally mixed with a considerable quantity of quartz-sand, or with powder of burnt clay. The smaller the amount of lime, potash, &c. present in the clay, the higher is the temperature which it sustains without fusing, and the more dense and solid is the baked mass obtained. But since it always remains porous, it is generally covered with a glaze consisting of an easily fusible glass usually containing oxide of lead. For stoneware and porcelain, a mixture is used of very infusible clay and fine quartz-sand, with a certain portion of gypsum or felspar. The lime present in the former or the potash in the latter, gives rise, at a high temperature, to incipient fusion and softening of the mass, by which means its porosity is in a great measure diminished. [On coloured glazes for porcelain and enamels, *vid.* Wächter, *Ann. Pharm.* 69, 99.]

B. Silicate of Alumina with Fluoride of Silicium or Fluoride of Aluminum.—*Topaz.*—Crystalline system, the right prismatic; $u^1 : u = 124° 20'$. Cleavage distinct, parallel to $p$; less distinct, parallel to the $a$-face of a rhombic octohedron. Specific gravity, from 3·4 to 3·6. Harder than quartz. Transparent, colourless, or with a slight tint only. Topaz is infusible before the blowpipe, but at a very high temperature becomes covered with small blisters, at the same time evolving hydrofluoric acid [or probably fluoride of silicium]. With borax it fuses slowly to a transparent glass; with phosphate of soda it forms a skeleton of silica, and fuses to a glass which becomes opalescent on cooling. With a small quantity of carbonate of soda, it yields—though with difficulty—a blistered opaque slag; with a larger proportion, it swells up and remains infusible. When ignited with solution of cobalt, it assumes a dirty blue colour. Hydrochloric acid does not decompose it. (Berzelius.)

| | | | | | Berzelius. | | | Klaproth. | |
|---|---|---|---|---|---|---|---|---|---|
| | At. | | *Topaz.* | | *a.* | *b.* | | *c.* | *d.* |
| $Al^2O^3$ ..... | 3 | .... | 154·2 | 57·41 | .... 57·45 | 58·38 | .... | 57·74 | 59 |
| $SiO^2$ ..... | 3 | .... | 93·0 | 34·62 | .... 34·24 | 34·01 | .... | 34·36 | 35 |
| F−O ..... | 2 | .... | 21·4 | 7·97 | .... 7·75 | 7·79 | .... | 7·77 | 5 |
| $Fe^2O^3$ ..... | | .... | | | .... | | .... | | trace |
| | 1 | .... | 268·6 | 100·00 | .... 99·44 | 100·18 | .... | 99·87 | 99 |

*a*, and *d*, are analyses of Topaz from the Schneckenstein;—*b* from the Brazils;—*c*, Pyrophysalite from Finbo. The simplest formula is the following: $(3Al^2O^3, 2SiO^2) + SiF^2 = 2(Al^2O^3, SiO^2) + Al^2O^3, SiF^2$. On this hypothesis one-third of the alumina would be combined with $SiF^2$ instead of with $SiO^2$.

*Pycnite*, a mineral resembling topaz, consists probably of $3(Al^2O^3, SiO^2) + SiF^2 = 2Al^2O^3, 3SiO^2 + Al^2O^3, SiF$.

| | *Pycnite.* | | Berzelius. | Klaproth. |
|---|---|---|---|---|
| $3Al^2O^3$ ..... | 154·2 | 51·47 | .... 51·00 | .... 49·5 |
| $4SiO^2$ ..... | 124·0 | 41·39 | .... 38·43 | .... 43·0 |
| $2F - O$ ..... | 21·4 | 7·14 | .... 8·84 | .... 4·0 |
| $Fe^2O^3$ ..... | | | .... | .... 1·0 |
| HO ..... | | | .... | .... 1·0 |
| | 299·6 | 100·00 | .... 98·27 | .... 98·5 |

C. Compounds of Silicate of Alumina with the Silicates of Potash, Soda, Lithia, Baryta, Strontia, Lime, Magnesia, Protoxide of Cerium, Yttria, Glucina, Protoxide of Manganese, and Protoxide of Iron.

Silica heated in the blast-furnace with alumina and baryta or strontia, fuses readily to a greenish-coloured porcelain; but with alumina and lime it does not fuse, unless the silica is in excess. (Kirwan.) A mixture of equal parts of lime, magnesia, alumina, and silica fuses to a glass. (Achard.)—One part of powdered spinell yields with 1·2 parts of silica a very hard, globular, grey mass, which does not adhere to the platinum crucible, and is not attacked even by the strongest acids till after fusion with carbonate of potash. (Abich, *Pogg.* 23, 307.)

*a. From 7 to 10 atoms of a stronger base with one atom of alumina.*

α. *Pennine.*—Occurs in acute rhombohedrons and short six-sided prisms. Harder than gypsum; flexible when in thin laminæ, but not elastic. Appears blackish green by reflected light; but, by transmitted light, emerald-green in the direction of the axis, and brown at right angles to it. It yields water when heated. Before the blowpipe it swells up and fuses at the edges to a yellowish white enamel. It dissolves in borax and microcosmic salt, forming a transparent glass coloured by iron; in the latter a skeleton of silica is also separated. With carbonate of soda it yields a brownish yellow slag. It dissolves in hydrochloric acid, with separation of silica in a floculent state, and with still greater facility in sulphuric acid. (Fröbel & Schweizer, *Pogg.* 50, 523.)

| | At. | *Pennine.* | | Schweizer. Mount Rosa. |
|---|---|---|---|---|
| MgO ..... | 25 .... | 500·0 | 31·70 .... | 33·04 to 32·34 |
| FeO ..... | 5 .... | 176·0 | 11·16 .... | 11·30 — 11·36 |
| $Al^2O^3$ ..... | 3 .... | 154·2 | 9·78 .... | 9·32 — 9·69 |
| $SiO^2$ ..... | 18 .... | 558·0 | 35·38 .... | 33·82 — 33·07 |
| HO ..... | 21 .... | 189·0 | 11·98 .... | 11·50 — 12·58 |
| | 1 .... | 1577·2 | 100·00 .... | 98·98 — 99·04 |

$10(MgO; FeO), 1Al^2O^3, 6SiO^2, 7Aq. = 5[(2MgO; FeO), SiO^2] + AlO^3, SiO^2 + 7Aq.$

β. *English Soap-stone*, according to Klaproth's analyses, consists of $7MgO, 1Al^2O^3, 8SiO^2, 10Aq.$; according to Svanberg, of $10MgO, 1Al^2O^3, 9SiO^2, 7Aq$.

*b. Six atoms of a stronger base with one atom of alumina.*

*α. Fornacite.*—A crystalline slag obtained in rhombic prisms from a lime-kiln heated with turf or peat; specific gravity between 2·85 and 3·11; crumbles to pieces between the fingers; fuses with difficulty at the edges only, and with intumescence; yields a jelly with hydrochloric acid; and contains 23·7 per cent. of lime, 11·8 of magnesia, 1·2 of protoxide of manganese, 4·0 of protoxide of iron, 14·5 of alumina, and 43·0 of silicic acid. (Reinsch, *J. pr. Chem.* 25, 110.) Its composition is nearly: $6(CaO; MgO; MnO; FeO,)\,1Al^2O^3, 5SiO^2$.

*β. Steatite from Snarum.* — $6MgO, 1(Fe^2O^3; Al^2O^3,)\,3SiO^2, 6Aq. = 2(3MgO, SiO^2) + Al^2O^3, SiO^2 + 6Aq.$

| | At. | | | | Hochstetter. | | Girowanski. |
|---|---|---|---|---|---|---|---|
| MgO | 36 | .... | 720·0 | 37·16 | 37·52 | .... | 37·9 |
| $Fe^2O^3$ | 1 | .... | 78·4 | 4·05 | 4·48 | .... | 3·1 |
| $Al^2O^3$ | 5 | .... | 257·0 | 13·27 | 12·52 | .... | 13·2 |
| $SiO^2$ | 18 | .... | 258·0 | 28·80 | 32·03 | .... | 30·2 |
| HO | 36 | .... | 324·0 | 16·72 | 16·19 | .... | 17·0 |
| | 1 | .... | 1637·4 | 100·00 | 102·74 | .... | 101·4 |

*γ. Pyrosklerite.*—$6(MgO; FeO), 1(Cr^2O^3; Al^2O^3,)4SiO^2, 4Aq. = 3(2MgO, SiO^2) + (Al^2O^3, SiO^2) + 4Aq.$ Has two planes of cleavage, one more and one less distinct, and at right angles to each other; specific gravity = 2·74; fracture uneven and splintered; softer than fluor-spar. (Green.) Fuses with difficulty before the blowpipe to a grey glass; with borax it yields a glass coloured green by chromium; and with solution of cobalt, a greyish mass. Pyrosklerite in the state of fine powder, is completely decomposed by concentrated hydrochloric acid, silica being separated, though not in the gelatinous state. (Von Kobell.)

| | At. | | *Pyrosklerite.* | | Von Kobell. |
|---|---|---|---|---|---|
| MgO | 79 | .... | 1580·0 | 33·30 | 31·62 |
| FeO | 5 | .... | 176·0 | 3·71 | 3·52 |
| $Cr^2O^3$ | 1 | .... | 80·2 | 1·69 | 1·43 |
| $Al^2O^3$ | 13 | .... | 668·2 | 14·08 | 13·50 |
| $SiO^2$ | 56 | .... | 1736·0 | 36·59 | 37·03 |
| HO | 56 | .... | 504·0 | 10·63 | 11·00 |
| | 1 | .... | 4744·4 | 100·00 | 98·10 |

*δ. Humboldtilite, Pure Sarcolite.*—Belongs to the square prismatic system. (*Fig.* 33); $p : e = 146°$. Sp. gr. from 2·91 to 3·1; of the same degree of hardness as apatite. Semi-transparent. Fuses readily before the blowpipe with slight evolution of gas-bubbles, and forms a blistered, translucent glass. It is easily decomposed, both before and after ignition, by hydrochloric acid, with separation of gelatinous silica. According to the analysis of Von Kobell, it approaches in composition to $2NaO, 17CaO, 4MgO, 1FeO$ (total 24), $- 4Al^2O^3, - 24SiO^2 = 3(2CaO, SiO^2) + Al^2O^3, 3SiO^2$.

*ε. Saponite.*—Soft and soapy when fresh; hardens or crumbles to powder in drying. White; unctuous to the touch; adheres to the tongue. Evolves water when heated. Before the blowpipe it shows traces of incipient fusion and blistering. Dissolves in borax, forming a turbid glass, and also in microcosmic salt, with separation of a skeleton of silica. (Svanberg).

| | At. | | *Saponite.* | | Svanberg. Svärdsjö. |
|---|---|---|---|---|---|
| CaO | .... | .... | | .... | 0·7 |
| MgO | 6 | .... | 120·0 | 27·69 | .... 25·5 |
| $Fe^2O^3$ | .... | .... | | .... | 2·0 |
| $Al^2O^3$ | 1 | .... | 51·4 | 11·86 | .... 9·4 |
| $SiO^2$ | 7 | .... | 217·0 | 50·07 | .... 50·8 |
| HO | 5 | .... | 45·0 | 10·38 | .... 10·5 |
| $6MgO, SiO^2 + Al^2O^3, SiO^2 + 5Aq.$ | 1 | .... | 433·4 | 100·00 | .... 99·9 |

*c. Five atoms of stronger base with one atom of alumina.*

*α. Ripidolite.*—$5(MgO; FeO), 1Al^2O^3, 3SiO^2, 4Aq.$ Related to chlorite: *Fig.* 132; $p : r = 120°$; $r : r^1 = 128° 42'$; $r : r^3 = 120°$; cleavage parallel to *p*. Specific gravity = 2·65. Blackish green. Exfoliates before the blowpipe, becomes white, and fuses at the edges to a white enamel; with borax it effervesces and forms a glass which is coloured by iron; with microcosmic salt it behaves in the same manner as uniaxial mica. It is perfectly decomposed by boiling with oil of vitriol. (Von Kobell.)

| | At. | | *Ripidolite.* | | Kobell. | Varrentrapp. Achmatowsk. | Brüel. Zillerthal. |
|---|---|---|---|---|---|---|---|
| MgO | 14 | .... | 280·0 | 32·69 | .... 34·40 | .... 33·97 | .... 32·56 |
| MnO | .... | | | | .... 0·53 | .... | .... 0·01 |
| FeO | 1 | .... | 35·2 | 4·11 | .... 3·85 | .... 4·37 | .... 5·97 |
| $Al^2O^3$ | 3 | .... | 154·2 | 18·01 | .... 17·14 | .... 16·97 | .... 16·97 |
| $SiO^2$ | 9 | .... | 279·0 | 32·58 | .... 31·14 | .... 30·38 | .... 31·47 |
| HO | 12 | .... | 108·0 | 12·61 | .... 12·20 | .... 12·63 | .... 12·42 |
| | 1 | .... | 856·4 | 100·00 | .... 99·26 | .... 98·32 | .... 99·40 |

The simplest formula: $6MgO, 1Al^2O^3, 3SiO^2 + 4Aq. = 2(3MgO, SiO^2) + Al^2O^3, SiO^2 + 4Aq.$, gives rather too much magnesia.

*β. Chonicrite.*—$10(CaO; MgO; FeO), 2Al^2O^3, 7SiO^2, 6Aq. = 5(2MgO, SiO^2, + 2(Al^2O^3, SiO^2) + 6Aq.$ Not crystalline, dense, with a conchoidal fracture, of specific gravity 2·91, and nearly as hard as calcspar. White and translucent. Chonicrite fuses with tolerable facility to a greyish white glass, evolving bubbles of gas at the same time; with solution of cobalt it forms a blue glass. It dissolves slowly in borax, yielding a glass slightly coloured by iron. It is easily decomposed by concentrated hydrochloric acid, silica being separated, but not in the usual gelatinous state. (Von Kobell.)

| | At. | | *Chonicrite.* | | Kobell. |
|---|---|---|---|---|---|
| CaO | 11 | .... | 308·0 | 12·85 | .... 12·60 |
| MgO | 28 | .... | 560·0 | 23·35 | .... 22·50 |
| FeO | 1 | .... | 35·2 | 1·47 | .... 1·46 |
| $Al^2O^3$ | 8 | .... | 411·2 | 17·14 | .... 17·12 |
| $SiO^2$ | 28 | .... | 868·0 | 36·19 | .... 35·69 |
| HO | 24 | .... | 216·0 | 9·00 | .... 9·00 |
| | 1 | .... | 2398·4 | 100·00 | .... 98·37 |

*d. Four atoms of stronger base with one atom of alumina.*

*α.* This includes the principal varieties of *Chlorite:* $4(MgO; FeO), 1(Al^2O^3; Fe^2O^3), 2SiO^2, 3Aq. = 4MgO, SiO^2 + Al^2O^3, SiO^2 + 3Aq.$ Crystalline system, the rhombohedral. Cleavage parallel to *p*, in slender but inelastic laminæ; specific gravity from 2·7 to 2·85; soft; dark green. Nearly fusible before the blowpipe. Decomposed by boiling oil of vitriol.

| | At. | *Chlorite.* | | Kobell. Zillerthal. | Kobell. Rauris. | Varrentrapp. St. Gotthard. |
|---|---|---|---|---|---|---|
| MgO | 3 | 60·0 | 25·47 | 24·89 | 14·69 | 17·09 |
| MnO | | | | 0·47 | 0·62 | |
| FeO | 1 | 35·2 | 14·94 | 15·23 | 26·87 | 28·79 |
| $Al^2O^3$ | 1 | 51·4 | 21·81 | 20·69 | 18·47 | 18·50 |
| $SiO^2$ | 2 | 62·0 | 26·32 | 27·32 | 26·06 | 25·37 |
| HO | 3 | 27·0 | 11·46 | 12·00 | 10·45 | 8·96 |
| Undecomposed residue | | | | | 2·24 | |
| | 1 | 235·6 | 100·00 | 100·60 | 99·40 | 98·71 |

In the chlorite of Rauris and in that of St. Gotthard, the silica amounts to rather more than 2 atoms. Chlorite from Pfitsch, analyzed by Varrentrapp, is $3MgO, 1(Al^2O^3; Fe^2O^3), 3SiO^2, 3HO$.

*β.* The principal varieties of *Uniaxial* or *Magnesia-mica* have likewise a similar composition*—$4MO, 1Al^2O^3, 4SiO^2 = 2(2MO, SiO^2) + Al^2O^3, 2SiO^2$. Under the symbol MO is included MgO, together with KO and FeO; a portion of the alumina is replaced by sesquioxide of iron; CaF and Aq. are also frequently present in small quantities. This mineral belongs to the rhombohedral system, and occurs in short, regular, six-sided prisms and very acute rhombohedrons. *Fig.* 135 and 153; cleavage very easy parallel to *p*; splits into very thin, elastic laminæ. Specific gravity from 2·78 to 2·94; hardness between that of gypsum and calcspar. Dark green and brown inclining to black, with a pearly metallic lustre on the cloven surfaces; translucent; has but one axis of polarization. When heated, it evolves a small quantity of water, and occasionally hydrofluoric acid. Fuses with tolerable facility, yielding a semi-opaque glass. It is but feebly acted on by hydrochloric acid; but sulphuric acid decomposes it completely.

| | At. | *Uniaxial Mica.* | | Kobell. Miask. | H. Rose. Miask. |
|---|---|---|---|---|---|
| KO | 4 | 198·8 | 8·44 | 8·58 | 5·61 |
| MgO | 19 | 380·0 | 16·14 | 16·15 | 15·70 |
| $M^2O^3$ | | | | | 0·63 |
| FeO | 9 | 316·8 | 13·46 | 9·36 | |
| $Fe^2O^3$ | 2 | 156·8 | 6·67 | 10·38 | 19·03 |
| $Al^2O^3$ | 6 | 308·4 | 13·10 | 12·83 | 12·67 |
| $SiO^2$ | 32 | 993·0 | 42·19 | 42·12 | 40·00 |
| HO | | | | 1·07 | |
| F—O | | | | | 2·10 |
| $TiO^2$ | | | | | 1·63 |
| | 1 | 2353·8 | 100·00 | 100·49 | 97·37 |

* ¶ Schaffhäutl (*Ann. Pharm.* 44, 325) compares compositions of the various micas one with another, by taking all the bases as one, and calculating them as $Al^2O^3$, and then combining them with the acid $SiO^3$. The following micas are thus compared:—

| | $Al^2O^3$ | $SiO^3$ | Formula. |
|---|---|---|---|
| Talc | 33·82 | 60·56 | $Al^2O^3$ $2SiO^3$ |
| Lithia Mica | 35·49 | 48·35 | $2Al^2O^3$ $3SiO^3$ |
| Biaxial Mica | 39·66 | 45·03 | $5Al^2O^3$ $6SiO^3$ |
| Magnesia Mica | 43·92 | 41·91 | $Al^2O^3$ $SiO^3$ |
| Chlorite | 55·30 | 31·38 | $5Al^2O^3$ $3SiO^3$ |
| Ripidolite | 61·73 | 26·31 | $2Al^2O^3$ $SiO^3$ |

From this it would appear that the composition of the micas ranges between $MO, 2SiO^3$ and $5MO, 3SiO^3$. ¶

| | At. | | | | | Von Kobell. Karosulk. |
|---|---|---|---|---|---|---|
| KO | 5 | .... | 236·0 | .... | 9·00 | .... 8·76 |
| MgO | 24 | .... | 480·0 | .... | 18·31 | .... 18·86 |
| $M^2O^3$ | | .... | | .... | | .... |
| FeO | 7 | .... | 246·4 | .... | 9·40 | .... 5·05 |
| $Fe^2O^3$ | | .... | | .... | | .... 4·50 |
| $Al^2O^3$ | 9 | .... | 462·6 | .... | 17·64 | .... 16·88 |
| $SiO^2$ | 36 | .... | 1116·0 | .... | 42·56 | .... 41·00 |
| HO | 9 | .... | 81·0 | .... | 3·09 | .... 4·30 |
| F—O | | .... | | .... | | .... trace |
| | 1 | .... | 2622·0 | .... | 100·00 | .... 99·35 |

| | At. | | | | | Von Kobell. Monroe. |
|---|---|---|---|---|---|---|
| KO | 8 | .... | 377·6 | .... | 10·82 | .... 10·83 |
| MgO | 37 | .... | 740·0 | .... | 21·20 | .... 21·54 |
| CaO | | .... | | .... | | .... |
| MnO | | .... | | .... | | .... |
| FeO | 3 | .... | 105·6 | .... | 3·03 | |
| $Fe^2O^3$ | 2 | .... | 156·8 | .... | 4·49 | 7·50 |
| $Al^2O^3$ | 10 | .... | 514·0 | .... | 14·73 | .... 16·16 |
| $SiO^2$ | 48 | .... | 1488·0 | .... | 42·64 | .... 40·00 |
| HO | 12 | .... | 108·0 | .... | 3·09 | .... 3·00 |
| F—O | | .... | | .... | | .... 0·53 |
| $TiO^2$ | | .... | | .... | | .... 0·20 |
| | 1 | .... | 3490·0 | .... | 100·00 | .... 99·76 |

| | At. | | | | | Svanberg. Sala. |
|---|---|---|---|---|---|---|
| KO | 4 | .... | 188·8 | .... | 5·61 | .... 6·03 |
| MgO | 44 | .... | 880·0 | .... | 26·17 | .... 25·97 |
| CaO | | .... | | .... | | .... 0·14 |
| MnO | | .... | | .... | | .... 1·06 |
| FeO | | .... | | .... | | .... |
| $Fe^2O^3$ | 3 | .... | 235·2 | .... | 6·99 | .... 7·11 |
| $Al^2O^3$ | 9 | .... | 462·6 | .... | 13·76 | .... 12·86 |
| $SiO^2$ | 48 | .... | 1488·0 | .... | 44·26 | .... 42·46 |
| HO | 12 | .... | 108·0 | .... | 3·21 | .... 3·17 |
| F—O | | .... | | .... | | .... 0·35 |
| | 1 | .... | 3362·6 | .... | 100·00 | .... 99·15 |

*Artificial Mica.*—Found in a peculiar slag containing small quantities of potash and lime, with a large proportion of magnesia. Six-sided tables, easily fusible. (Mitscherlich, *Ann. Chim. Phys.* 24, 355.)

γ. *Orthite.*—4(CaO; MgO; CeO; LaO; YO; MnO; FeO), 1($Fe^2O^3$; $Al^2O^3$), $4SiO^2$, with very variable proportions of water = 4(CaO; &c.), $2SiO^2$+($Fe^2O^3$; $Al^2O^3$), $2SiO^2$+$x$Aq. Specific gravity, from 3·28 to 3·64; as hard as quartz, with a conchoidal fracture. Blackish grey, or in some cases jet-black; opaque. Yields water when heated, and emits a faint phosphorescent light. Before the blowpipe, it swells up, fuses, and boils, forming a blackish blistered glass. With borax or microcosmic salt it yields a glass coloured by iron. Fuses perfectly with a small quantity of carbonate of soda, but with a larger proportion it swells up and forms a slag. Hydrochloric acid dissolves it, if not previously ignited, and converts it into a gelatinous mass.

| | Berzelius. Finbo. | Gottliebsgang. | Berlin. Ytterby. | Th. Scheerer. Fillefjeld. |
|---|---|---|---|---|
| KO, NaO .... | .... | .... | 0·61 .... | |
| CaO..... | 4·87 .... | 7·84 .... | 5·48 .... | 10·42 |
| MgO ..... | .... | .... | 0·61 .... | 0·86 |
| CeO..... | 17·39 .... | 19·44 .... | 4·98 } .... | 21·43 |
| LaO ..... | .... | .... | } | |
| YO ..... | 3·80 .... | 3·44 .... | 29·81 .... | 1·91 |
| MnO ..... | 1·36 .... | 3·40 .... | .... | 8·85 |
| FeO..... | 11·42 .... | 12·44 .... | 9·06 .... | 14·90 |
| $Al^2O^3$ ..... | 14·00 .... | 14·80 .... | 8·18 .... | 14·26 |
| $SiO^2$ ..... | 36·25 .... | 32·00 .... | 36·24 .... | 34·93 |
| HO ..... | 8·70 .... | 5·36 .... | 4·59 .... | 0·52 |
| | 97·79 .... | 98·72 .... | 99·56 .... | 100·08 |

In the third analysis, the protoxides of manganese and iron were probably reckoned wholly, and in the fourth partly, as sesquioxides.

*e. Three atoms of stronger base with one atom of alumina.*

*α. Gehlenite.*—Rectangular four-sided prisms. Cleavage parallel to *p*. Specific gravity from 2·9 to 3·0. Harder than apatite. Very difficult to fuse before the blowpipe; difficultly soluble in borax or microcosmic salt. Gehlenite, both before and after ignition, is completely decomposed by hydrochloric acid, with separation of gelatinous silica.

| | At. | *Gehlenite.* | | Kobell. | Fuchs. | Kühn. |
|---|---|---|---|---|---|---|
| CaO..... | 24 .... | 672·0 | 37·76 .... | 37·4 .... | 35·30 .... | 36·97 |
| MgO ..... | 3 .... | 60·0 | 3·37 .... | 3·4 .... | .... | 2·99 |
| FeO..... | .... | | .... | 4·4 } .... | .... | |
| $Fe^2O^3$ ..... | 1 .... | 78·4 | 4·41 .... | } .... | 6·56 .... | 7·30 |
| $Al^2O^3$ ..... | 8 .... | 411·2 | 23·11 .... | 21·4 .... | 24·80 .... | 17·79 |
| $SiO^2$ ..... | 18 .... | 558·0 | 31·35 .... | 31·0 .... | 29·64 .... | 30·47 |
| HO ..... | .... | | .... | 2·0 .... | 3·30 .... | 3·62 |
| | 1 .... | 1779·6 | 100·00 .... | 99·6 .... | 99·60 .... | 99·14 |

Hence the formula for Gehlenite should be: $3(CaO; MgO), 1(Fe^2O^3 Al^2O^3), 2SiO^2$. Kühn gives the formula: $4(2CaO, SiO^2) + (2Al^2O^3, SiO^2) + 2HO$. But if the iron which it contains were in the state of ferrous or ferroso-ferric oxide, this formula would not be correct. If the water be really an essential constituent, it amounts to half an atom for every 2 atoms of silica.

*β. Euclase.*—The annexed formula is but remotely approximative, and therefore doubtful: $3GO, 1Al^2O^3, 2SiO^2 = 3GO, SiO^2 + Al^2O^3, SiO^2$. Crystalline system, the oblique prismatic. *Fig.* 86, with numerous other faces. $i$ : angle between $u$ and $u = 130° 8'$; $i : a = 126° 51'$; $u^1 : u = 65° 42'$; $u : t = 122° 51'$; $a : t = 126° 51'$; cleavage very easy, parallel to $t$; less easy, parallel to $m$. (Hauy.) Specific gravity = 3·06; harder than topaz. Swells up before the blowpipe, forming a cauliflower-like mass, and fuses at the extreme edges to a white enamel. Dissolves very slowly in borax, with some degree of effervescence, forming a transparent glass. With microcosmic salt it yields an insoluble skeleton of silica, and a transparent glass which becomes opalescent on cooling. With a small quantity of carbonate of soda, it gives a turbid glass; and with a larger proportion, a transparent glass. It is not acted on by acids.

| | At. | | *Eudiase.* | | | Berzelius. |
|---|---|---|---|---|---|---|
| GO ..... | 3 | .... | 38·1 | 25·15 | .... | 21·78 |
| $Fe^2O^3$ ..... | | .... | | | .... | 2·22 |
| $Al^2O^3$ ..... | 1 | .... | 51·4 | 33·93 | .... | 30·56 |
| $SiO^2$ ..... | 2 | .... | 62·0 | 40·92 | .... | 43·22 |
| $SnO^2$ ..... | | .... | | | .... | 0·70 |
| | 1 | .... | 151·5 | 100·00 | .... | 98·48 |

γ. *Vesuvian, Idocrase.*—$3(CaO; MgO; MnO; FeO), 1(Fe^2O^3; Al^2O^3), 3SiO^2 = 3CaO, 2SiO^2 + Al^2O^3, SiO^2$. Belongs to the square prismatic system. *Fig.* 28, 31, 39, and other forms. $p : e = 142° 54'$; cleavage imperfect, parallel to *p* and *q*. (Hauy.) Specific gravity = 3·31 to 3·45; harder than felspar. Transparent, yellowish green, &c. Swells up and fuses readily before the blowpipe, forming a yellowish green or brownish glass. Dissolves easily in borax and microcosmic salt, forming a glass coloured by iron; the glass formed with microcosmic salt likewise contains a skeleton of silica, and becomes opalescent on cooling. With a small quantity of carbonate of soda it fuses, though with difficulty, and forms a glass; with a larger quantity, it forms a slag-like mass. (Berzelius.) Vesuvian from Egg, which has a specific gravity of 3·45, yields, after fusion in a crucible, a glass whose density is only from 2·944 to 2·965; and that from the banks of the Wilui in Siberia, a glass which resembles the unfused mineral in colour and translucency, but is softer. (Magnus.) Vesuvian before fusion is but partially decomposed by hydrochloric acid; but after fusion that acid decomposes it completely, separating gelatinous silica. (Von Kobell; see also I., 102.)

| | At. | | *Vesuvian.* | | | Karsten. Piedmont. | Karsten. Vesuvius. | | Magnus. Slato. |
|---|---|---|---|---|---|---|---|---|---|
| CaO..... | 49 | .... | 1372·0 | 33·26 | .... | 33·85 | 33·71 | .... | 35·79 |
| MgO ..... | 5 | .... | 100·0 | 2·43 | .... | 2·70 | 3·10 | .... | 0·77 |
| MnO ..... | | .... | | | .... | 0·75 | 0·10 | .... | 1·49 |
| FeO..... | | .... | | | .... | | | .... | 4·67 |
| $Fe^2O^3$ ..... | 2 | .... | 156·8 | 3·80 | .... | 4·30 | 6·25 | | |
| $Al^2O^3$ ..... | 16 | .... | 822·4 | 19·93 | .... | 18·10 | 18·50 | .... | 18·11 |
| $SiO^2$ ..... | 54 | .... | 1674·0 | 40·58 | .... | 39·25 | 37·50 | .... | 37·18 |
| | 1 | .... | 4125·2 | 100·00 | .... | 98·95 | 99·16 | .... | 98·01 |

Most of the analyses of vesuvian do not yield results exactly corresponding to the formula; for if the whole of the iron is reckoned as sesquioxide, they give too large a proportion of strong base or too small a quantity of silica. Some varieties of vesuvian contain soda; others, more or less phosphoric acid.

*Artificial Vesuvian* was found by Berthier (*Ann. Chim. Phys.* 33, 172) in the slag of an iron-smelting furnace fed with coke.

δ. *Garnet.*—Has the same composition as vesuvian, and is dimorphous with it.—Belongs to the regular system of crystallization; most frequently occurring in rhomboidal dodecahedrons, and in octohedrons like those of leucite (*Fig.* 3 and 11); cleavage imperfect, parallel to *d*. Specific gravity from 3·4 to 4·3; somewhat harder than quartz; transparent, and of various colours. Before the blowpipe garnet fuses readily and tranquilly, forming a transparent glass; with fluxes it behaves like vesuvian. The glass obtained by fusing garnet has a lower specific gravity than the mineral itself. The specific gravity of garnet from Greenland diminishes on fusion from 3·9 to 3·05; that of the garnet

(*Grossular*) from the Wilui, from 3·63 to 2·95; the latter glass corresponds with the fused vesuvian of the Wilui, both in its physical and chemical characters. (See I., 106.)

Garnet in its native state is not acted on by hydrochloric acid, or but partially when it contains a large proportion of lime; but after fusion it is completely decomposed, with separation of gelatinous silica; with garnets which contain a large quantity of lime, a red heat is sufficient for this purpose. (Kobell.)

All garnets may be considered—particularly with reference to the experiments of Trolle Wachtmeister—as mixtures in variable proportions of the following varieties:

| | |
|---|---|
| 1. $3CaO, Al^2O^3, 3SiO^2$; | 2. $3MgO, Al^2O^3, 3SiO^2$; |
| 3. $3MnO, Al^2O^3, 3SiO^2$; | 4. $3FeO, Al^2O^3, 3SiO^2$; |
| 5. $3CaO, Fe^2O^3, 3SiO^2$; | 6. $3MgO, Fe^2O^3, 3SiO^2$; |
| 7. $3MnO, Fe^2O^3, 3SiO^2$; | 8. $3FeO, Fe^2O^3, 3SiO^2$. |

The compound 1 (*calcareous alumina-garnet*) predominates in *Cinnamon-stone* (*Grossular*) and in the white garnet of Tellemarken; the compound 2 (*magnesio-alumina-garnet*) in the black garnet of Arendal; the compound 3 (*manganesio-alumina-garnet*) in a variety of garnet from North America, examined by Seybert, and in the garnet of Broddbo; the compound 4 (*ferruginous alumina-garnet*) in the oriental *Almandine* and other red varieties of precious garnet; the compound 5 (*calcareous iron garnet*) in the ordinary yellow, brown, and black garnet, and also in *Melanite;* the compounds 6, 7, and 8 are not found to predominate in any of the varieties of garnet. *Pyrope,* which is principally composed of the compounds 1, 2, and 5, is characterized by containing chromium, which, in the form of sesquioxide, probably replaces a portion of the alumina.

1. *Allanite, Cerine.*—$3(CaO; CeO; FeO), 1(Fe^2O^3; Al^2O^3), 3SiO^2 = 3(CaO; CeO; FeO), 2SiO^2 + (Fe^2O^3; Al^2O^3), SiO^2$. Specific gravity from 3·4 to 3·8; harder than apatite; fracture conchoidal. Jet-black and opaque. Fuses to a black glass, with slight evolution of gas bubbles. Most varieties are decomposed by hydrochloric acid, with formation of a jelly. The allanite of Snarum, however, is but very imperfectly decomposed; and that from the mines of Bastnäs resists the action of the acid altogether.—The following calculation is founded on Stromeyer's analysis. Hermann regards the mineral from Miask, which he analysed, as orthite, although its composition corresponds rather to that of allanite:

| | At. | *Allanite.* | | Stromeyer. Iglorsoit. | Hermann. Miask. | Th. Scheerer. Jotunfjeld. | Snarum. |
|---|---|---|---|---|---|---|---|
| CaO | 6 | 168·0 | 10·40 | 11·08 | 9·25 | 12·02 | 11·75 |
| MgO | | | | | 2·06 | 0·78 | 0·56 |
| CeO | 7 | 378·0 | 23·40 | 21·60 | 17·39 | 13·34 | 13·73 |
| LaO | | | | | | 5·80 | 7·50 |
| MnO | | | | 0·40 | 2·37 | 0·98 | |
| FeO | 5 | 176·0 | 10·89 | 15·10 | 13·03 | 15·55 | 15·51 |
| $Fe^2O^3$ | 1 | 78·4 | 4·85 | | | | |
| $Al^2O^3$ | 5 | 257·0 | 15·91 | 15·23 | 18·21 | 16·23 | 16·40 |
| $SiO^2$ | 18 | 558·0 | 34·55 | 33·02 | 35·49 | 35·15 | 34·00 |
| HO | | | | 3·00 | 2·00 | 0·50 | |
| | 1 | 1615·4 | 100·00 | 99·43 | 99·80 | 100·35 | 99·45 |

2. *Beryl, Emerald, Davidsonite.*—$3GO, 1Al^2O^3, 6SiO^2 = 3(GO, SiO^2), + Al^2O^3, 3SiO^2$.—Crystalline system, the rhombohedral (B, *a*, I., 16). (*F*

135, 136, 187, 140, and other forms); $p : r$ (*Fig.* 136) = 135°; $p : r$ (*Fig.* 137) = 150; cleavage easy parallel to $p$, less easy parallel to $s$. Specific gravity from 1·58 to 2·73; harder than quartz. Before the blowpipe it fuses with difficulty, and at the edges only, to a turbid blistered glass; with borax or carbonate of soda it yields a transparent glass, which becomes turbid on cooling; with microcosmic salt it likewise forms, without any separation of silica, a clear glass which becomes turbid as it cools. Not decomposed by acids, or but partially by sulphuric acid after strong ignition. When exposed to the heat of a blast-furnace, with an equal weight of white marble in a charcoal crucible, it yields, according to Berthier, a transparent glass, the powder of which is perfectly decomposed by hydrochloric or sulphuric acid, with separation of gelatinous silica.

| | At. | *Beryl.* | | Vauquelin. Brazil. | Berzelius. Broddbo. | Th. Scheerer. Modum. | C. Gmelin. Limoges. |
|---|---|---|---|---|---|---|---|
| CaO | | | | 0·25 | | 0·18 | |
| GO | 3 | 38·1 | 13·83 | 12·50 | 13·13 | 12·56 | 13·51 |
| $Cr^2O^3$ | | | | 0·30 | $TaO^3$ 0·72 | | |
| $Fe^2O^3$ | | | | 1·00 | 0·72 | 0·53 | |
| $Al^2O^3$ | 1 | 51·4 | 18·66 | 15·75 | 17·60 | 19·64 | 17·63 |
| $SiO^2$ | 6 | 186·0 | 67·51 | 68·50 | 68·35 | 67·00 | 67·54 |
| | 1 | 275·5 | 100·00 | 98·30 | 100·52 | 99·91 | 99·68 |

*f. Two atoms of stronger base with one atom of alumina.*

$\alpha$. *Prehnite.* — $2CaO, —1Al^2O^3, —3SiO^2, —1Aq. = 2(CaO, SiO^2) + Al^2O^3, SiO^2 + Aq.$—Crystalline system, the right prismatic; *Fig.* 61, 49, 70, and others; $u^1 : u = 102° 40'$; $p : i = 155° 23'$. Cleavage distinct, parallel to $p$; less distinct parallel to $u$. (Hauy.) Specific gravity = 2·92; harder than felspar. Translucent, and of a light colour. When heated, it loses water but does not become opaque. Fuses before the blowpipe to a blistered glass, with rapid evolution of gas bubbles. In the native state it is but imperfectly acted on by acids; but after strong ignition or fusion, acids decompose it completely, forming a jelly. (Von Kobell.)

| | At. | | | Walmstedt. Dumbarton. | Walmstedt. Edelforfs. | Regnault. B. d'Oisans. |
|---|---|---|---|---|---|---|
| CaO | 2 | 56·0 | 26·74 | 26·43 | 26·28 | 23·47 |
| $Mn^2O^3$ | | | | | 0·15 | |
| $Fe^2O^3$ | | | | 0·74 | 6·81 | 4·61 |
| $Al^2O^3$ | 1 | 51·4 | 24·55 | 24·26 | 19·30 | 23·44 |
| $SiO^2$ | 3 | 93·0 | 44·41 | 44·10 | 43·03 | 44·50 |
| HO | 1 | 9·0 | 4·30 | 4·18 | 4·43 | 4·44 |
| | 1 | 209·4 | 100·00 | 99·71 | 100·00 | 100·46 |

$\beta$. Many varieties of *Uniaxial* or *Magnesia-mica* come under this head (*vid*, III., 423).—$2MO, —Al^2O^3, —3SiO^2 = 2(MO, SiO^2) + Al^2O^3, SiO^2$.—MO represents MgO with KO, CaO, and FeO; a portion of $Al^2O^3$ is replaced by $Fe^2O^3$. Mica contains small quantities of CaF and water, but it has not been ascertained whether these substances are essential to its composition.

| | At. | *Uniaxial Mica.* | | Svanberg. Pargas. |
|---|---|---|---|---|
| KO | 5 | 236·0 | 9·26 | 8·45 |
| CaO | | | | 0·26 |
| MgO | 13 | 260·0 | 10·20 | 10·27 |
| MnO | | | | 0·75 |
| FeO | 6 | 211·2 | 8·29 | |
| $Fe^2O^3$ | 1 | 78·4 | 3·08 | 10·39 |
| $Al^2O^3$ | 11 | 565·4 | 22·19 | 21·68 |
| $SiO^2$ | 36 | 1116·0 | 43·80 | 42·58 |
| HO | 9 | 81·0 | 3·18 | 3·35 |
| CaF | | | | 1·06 |
| | 1 | 2548·0 | 100·00 | 98·79 |

| | At. | | | Svanberg. Rosendas. |
|---|---|---|---|---|
| KO | 3 | 141·6 | 4·26 | 4·05 |
| CaO | 1 | 28·0 | 0·84 | 0·90 |
| MgO | 18 | 360·0 | 10·82 | 11·26 |
| MnO | | | | 0·44 |
| FeO | 10 | 352·0 | 10·58 | 20·71 |
| $Fe^2O^3$ | 5 | 392·0 | 11·78 | |
| $Al^2O^3$ | 11 | 565·4 | 16·99 | 16·85 |
| $SiO^2$ | 48 | 1488·0 | 44·73 | 44·41 |
| HO | | | | 1·13 |
| CaF | | | | 0·84 |
| | 1 | 3327·0 | 100·00 | 100·59 |

*γ. Tachylyte* or *Conchoidal Augite.*—Amorphous; with conchoidal fracture; specific gravity 2·714. Black. Fuses very readily to an opaque glass. Concentrated hydrochloric acid decomposes it completely in the cold. According to C. Gmelin's analysis it appears to consist of about 2(KO; NaO; CaO; MgO; MnO; FeO), 1($Fe^2O^3$; $Al^2O^3$), $4SiO^2$.

*g. 3 atoms of stronger base with 2 atoms of alumina.*

*α. Epidote.*—3(CaO; MgO; MnO; FeO), 2($Fe^2O^3$; $Al^2O^3$), $4SiO^2$ = 3(CaO; MgO; MnO; FeO), $2SiO^2$ + 2($Al^2O^3$, $SiO^2$).—Belongs to the modified oblique prismatic (one and two-membered) system. Primary form, a right rhomboidal prism; angles of the lateral edges = 114° 37′ and 65° 23′. (Hauy.) According to Brooke, this form, which is found in pistacite, is diversified in zoisite which occurs in oblique rhombic prisms. *Fig.* 87, with other faces; $u^1 : u$ = 116° 30′, &c. Specific gravity from 3·0 to 3·5; harder than felspar.

1. *Calcareous Epidote, Zoisite.*—Generally consists of $3CaO, 2Al^2O^3, 4SiO^2$. Kühn gives 2(2CaO, &c., $SiO^2$) + 2($Al^2O^3 1\frac{1}{2}SiO^2$) + $Al^2O^3$, $SiO^2$. Slightly coloured. Swells up before the blowpipe, evolves bubbles of gas, and fuses at the edges to a transparent glass. Swells up with borax, and dissolves in it, forming a clear glass. In microcosmic salt it likewise swells up and dissolves readily, with effervescence and separation of a skeleton of silica. With a very small quantity of carbonate of soda it forms a pale green glass; with a larger quantity, it swells up to a white infusible mass. With solution of cobalt it produces a blue glass. (Berzelius.) It is partially decomposed by hydrochloric acid; but after ignition or fusion, that acid decomposes it perfectly, with formation of a jelly.

| | At. | | | | Stromeyer. Stirring. |
|---|---|---|---|---|---|
| KO & NaO | | | | | 0·89 |
| CaO | 3 | 84·0 | 27·03 | | 23·86 |
| MnO | | | | | 0·17 |
| FeO | | | | | 2·24 |
| $Al^2O^3$ | 2 | 102·8 | 33·07 | | 31·97 |
| $SiO^2$ | 4 | 124·0 | 39·90 | | 39·92 |
| HO | | | | | 0·95 |
| | 1 | 310·8 | 100·00 | | 100·00 |

| | Geffken. Fichtelgebirg. | | Kühn. Zwiesel. |
|---|---|---|---|
| CaO | 18·85 | | 22·90 |
| MnO | 7·55 | MgO | 1·95 |
| FeO | 4·24 | $Fe^2O^3$ | 4·35 |
| $Al^2O^3$ | 29·83 | | 30·63 |
| $SiO^2$ | 40·03 | | 40·17 |
| | 100·50 | | 100·00 |

2. *Ferruginous Epidote, Pistacite.*—$6(2CaO, SiO^2) + 3(Al^2O^3, 1\frac{1}{2}SiO^2) + (Al^2O^3, SiO^2)$. (Kühn.)—In this mineral a larger quantity of the lime is replaced by protoxide of iron, and a large proportion of the alumina by sesquioxide of iron. Transparent; green. Before the blowpipe it fuses at the edges, and subsequently swells up, forming a dark brown mass, which, by exposure to a more powerful blast, becomes black and somewhat rounded. (Berzelius.)

| | At. | | | | Descotils. Dauphinée. | | Beudant. St. Jean. | | Vauquelin. Arendal. | | Kühn. Arendal. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CaO | 10 | 280·0 | 14·37 | | 14·0 | | 16·2 | | 15·0 | | 23·07 |
| $Mn^2O^3$ | | | | | 1·5 | | | | 1·5 | MgO | 0·53 |
| FeO | 8 | 281·6 | 14·45 | | | | | | | | |
| $Fe^2O^3$ | 1 | 78·4 | 4·02 | | 17·0 | | 14·0 | | 24·0 | | 16·72 |
| $Al^2O^3$ | 11 | 565·4 | 29·00 | | 27·0 | | 28·9 | | 21·0 | | 21·72 |
| $SiO^2$ | 24 | 744·0 | 38·16 | | 37·0 | | 40·9 | | 37·0 | | 36·68 |
| | 1 | 1949·4 | 100·00 | | 96·5 | | 100·0 | | 98·5 | | 98·72 |

3. *Manganesian Epidote.*—In this mineral, protoxide of manganese replaces the greater part of the lime, and sesquioxide of manganese and sesquioxide of iron a portion of the alumina. The analyses agree so little together that a correct calculation of the formula is impossible; the results obtained by Cordier correspond to about $28CaO, 9MnO$;—$1Mn^2O^3, 8Fe^2O^3, 9Al^2O^3$;—$36SiO^2$.

| | Cordier. | | Hartwall. |
|---|---|---|---|
| CaO | 14·5 | | 21·65 |
| MgO | | | 1·82 |
| MnO | 12·0 | | |
| $Mn^2O^3$ | | | 14·08 |
| $Fe^2O^3$ | 19·5 | | 6·60 |
| $Al^2O^3$ | 15·0 | | 17·65 |
| $SiO^2$ | 33·5 | | 38·47 |
| | 94·5 | | 100·27 |

*β. Mejonite.*—Crystalline system, the square prismatic. *Fig.* 29, without the *p*-face; $r : e = 121° 45'$; cleavage parallel to *p* and *r*. Specific gravity = 2·65. Transparent and colourless. Swells up strongly before the blow-

pipe, and fuses to a blistered, coloured glass. (Berzelius.) It is perfectly decomposed by hydrochloric acid, with formation of a jelly. Has apparently the same composition as zoisite, except that a small portion of the lime is replaced by potash and soda.

| | At. | | | | Stromeyer. Vesuvius. | L. Gmelin. Vesuvius. |
|---|---|---|---|---|---|---|
| NaO, KO | | | | | 1·81 | 2·4 |
| CaO | 3 | 84·0 | 27·03 | | 24·25 | 22·1 |
| $Fe^2O^3$ | | | | | 0·18 | 1·0 |
| $Al^2O^3$ | 2 | 102·8 | 33·07 | | 32·73 | 30·6 |
| $SiO^2$ | 1 | 124·0 | 39·90 | | 40·53 | 40·8 |
| | 1 | 310·8 | 100·00 | | 99·50 | 96·9 |

*γ. Weissite*, or *Scaly Triklasite.*—Appears, according to the analyses of Trolle Wachtmeister, to consist of 3(KO; NaO; MgO; ZnO; MnO; FeO),—2 $Al^2O^3$,—8$SiO^2$.

*δ. Phacolite.*—Resembles chabasite in its crystalline form; before the blowpipe it behaves like other zeolites. According to Anderson's analysis (*N. Ed. Phil. J.* 34, 23), it appears to contain 3CaO, 2$Al^2O^3$, 8$SiO^2$, 10Aq.

*h. One atom of stronger base with one atom of alumina.*

*α.* MO, $Al^2O^3$, 2$SiO^2$ = MO, $SiO^2$ + $Al^2O^3$, $SiO^2$.

The symbol MO comprehends KO, NaO, CaO, MgO, &c.

1. *Artificial Potash-compound.*—If a mixture of 2 parts of alumina and 3 parts of silica is fused with 15 parts or more of carbonate of potash, and the mass when cold is reduced to powder and exhausted with water, a compound corresponding to the above formula remains undissolved; it is decomposed by hydrochloric acid. (Berzelius.)

| | | | Berzelius. |
|---|---|---|---|
| KO | 47·2 | 29·39 | 28·65 |
| $Al^2O^3$ | 51·4 | 32·01 | 32·04 |
| 2$SiO^2$ | 62·0 | 38·60 | 39·31 |
| | 160·6 | 100·00 | 100·00 |

2. *Artificial Soda-compound.*—Obtained in the same manner, and precisely similar in constitution. (Berzelius.) NaO, $SiO^2$ + $Al^2O^3$, $SiO^2$.

3. *Elaeolite, Nepheline.*—Crystalline system, the hexagonal (B. *a*, I., 16.) (*Fig.* 135 and 137); $p : r = 151° 53'$. Specific gravity from 2·5 to 2·6. Harder than apatite. Transparent and colourless. Before the blowpipe, it fuses to a colourless blistered glass; dissolves slowly in borax, yielding a colourless glass; slowly also in microcosmic salt, with separation of a skeleton of silica, forming a glass which becomes opalescent on cooling. With solution of cobalt it turns blue at the fused edges. (Berzelius.) Fragments of the mineral become turbid in nitric acid. In the state of powder, it is completely decomposed by hydrochloric acid, and converted into a gelatinous mass.

*a.* The most simple formula for nepheline would be: (KO; NaO), $SiO^2$ + $Al^2O^3$, $SiO^2$; or more fully, (KO; $SiO^2$) 4(NaO, $SiO^2$) + 5($Al^2O^3$, $SiO^2$).

*b.* The following formula (resembling that given by Th. Scheerer) corresponds, however, more strictly with most of the analyses:

$(KO, 2SiO^2) + 4(NaO, SiO^2) + 5(Al^2O^3, SiO^2)$. According to this formula, 5 atoms of stronger base and 5 atoms of alumina are combined not with 10, but with 11 atoms of silicic acid.

| | Calculation according to formula *a*. | | | | According to formula *b*. | | | |
|---|---|---|---|---|---|---|---|---|
| | At. | | | | At. | | | |
| KO | 1 | 47·2 | 6·39 | | 1 | 47·2 | 6·13 | |
| NaO | 4 | 124·8 | 16·89 | | 4 | 124·8 | 16·21 | |
| $Al^2O^3$ | 5 | 257·0 | 34·77 | | 5 | 257·0 | 33·37 | |
| $SiO^2$ | 10 | 310·0 | 41·95 | | 11 | 341·0 | 44·29 | |
| | 1 | 739·0 | 100·00 | | 1 | 770·0 | 100·00 | |

| | *Nepheline.* | | | | *Elaeolite.* | | | |
|---|---|---|---|---|---|---|---|---|
| | Th. Scheerer. | | Bromeis. | | Th. Scheerer. | | | |
| | Katzenbuckel. | Vesuvius. | Miask. | | Miask. | Brevig. | Fredriksvärn. | |
| KO | 5·60 | 4·52 | 6·43 | | 5·69 | 5·10 | 5·45 | |
| NaO | 15·83 | 15·91 | 15·14 | | 15·70 | 15·67 | 15·95 | |
| CaO | 0·84 | 2·01 | 0·33 | | 0·26 | 0·28 | 0·33 | |
| MgO | | trace | 0·61 | | trace | | | |
| $Fe^2O^3$ | 1·07 | 0·44 | trace | | 0·57 | 0·86 | 0·45 | |
| $Al^2O^3$ | 32·31 | 34·06 | 34·06 | | 33·12 | 32·14 | 32·63 | |
| $SiO^2$ | 43·70 | 44·04 | 42·42 | | 44·07 | 44·59 | 45·31 | |
| HO | 1·39 | 0·21 | 0·46 | | 0·90 | 2·05 | 0·60 | |
| HCl | | 0·14 | 0·04 | | 0·06 | | | |
| $SO^3$ | | 0·05 | | | 0·07 | | | |
| | 100·74 | 101·38 | 99·49 | | 100·44 | 100·69 | 100·72 | |

4. *Wernerite, Scapolite.*—$1CaO, 1Al^2O^3, 2SiO^2 = CaO, SiO^2 + Al^2O^3, SiO^2$. —Crystalline system, the square prismatic. *Fig.* 39 without the *p*-face; $e : r$ about 121°; cleavage parallel to *q* and *r*. Specific gravity from 2·7 to 2·8. Softer than felspar. Colourless and translucent. Fuses before the blowpipe and swells up to a translucent mass, which is no longer fusible. Dissolves in borax or microcosmic salt, with continued effervescence, forming a transparent glass. With a small quantity of carbonate of soda, it yields a clear glass, which, on a larger addition of the carbonate, becomes infusible. With solution of cobalt it gives a blue glass. (Berzelius.) When finely pounded, it is perfectly decomposed by hydrochloric acid, without forming a siliceous jelly (thereby distinguished from Mejonite).

| | | *Wernerite.* | | Walmstedt. | Nordenskiold. |
|---|---|---|---|---|---|
| | At. | | | Tunaberg. | Pargas. |
| CaO | 1 | 28·0 | 19·80 | 19·37 | 18·96 |
| FeO | | | | 0·61 | |
| $Al^2O^3$ | 1 | 51·4 | 36·35 | 35·28 | 35·43 |
| $SiO^2$ | 2 | 62·0 | 43·85 | 43·83 | 43·83 |
| HO | | | | | 1·03 |
| | 1 | 141·4 | 100·00 | 99·09 | 99·25 |

5. *Anorthite.*—Crystalline system, the doubly oblique prismatic. Primary form; *Fig.* 121; $y : u = 94° 12'$; $y : v = 110° 57'$; $u : v = 117° 28'$; cleavage parallel to *y* and *u*. Specific gravity = 2·763. (G. Rose.) Harder than apatite. In the rest of its characters it resembles felspar. Before the blowpipe it behaves like felspar, but yields with carbonate of soda, in every proportion, a white enamel—never a transparent glass. (Berzelius.) Concentrated hydrochloric acid completely decomposes it without forming a jelly. (G. Rose.) It has the same

formula as scapolite, excepting that small portions of the lime are replaced by magnesia, potash, and soda. To this division also belongs Nordenskiold's *Amphodelite* of Lojo, which has two planes of cleavage, inclined to each other at an angle of 94° 19′. Specific gravity, 2·763. Also the *Diploite* or *Latrobite* of Greenland, which belongs to the doubly oblique prismatic system. According to Brooke, its two planes of cleavage also make an angle of 93° 30′ with each other; according to Breithaupt, the angle is about 95°. Specific gravity = 2·72 (Breithaupt), = 2·8 (Brooke.) The following result is the mean of two analyses of Latrobite.

| | At. | | *Anorthite.* | | | G. Rose. Vesuvius. |
|---|---|---|---|---|---|---|
| KO | | .... | | | .... | |
| NaO | | .... | | | .... | |
| CaO | 1 | .... | 28·0 | 19·80 | .... | 15·68 |
| MgO | | .... | | | .... | 5·26 |
| $Fe^2O^3$ | | .... | | | .... | 0·74 |
| $Al^2O^3$ | 1 | .... | 51·4 | 36·35 | .... | 34·46 |
| $SiO^2$ | 2 | .... | 62·0 | 43·85 | .... | 44·49 |
| | 1 | .... | 141·4 | 100·00 | .... | 100·63 |

| | *a.* | Abich. Vesuvius. | *b.* | | Nordenskiold. *Amphodelite.* | | C. Gmelin. *Latrobite.* |
|---|---|---|---|---|---|---|---|
| KO | 0·25 | .... | 0·88 | .... | | .... | 6·57 |
| Nao | 0·27 | .... | trace | | | | |
| CaO | 19·02 | .... | 18·07 | .... | 10·15 | .... | 9·03 |
| MgO | 0·56 | .... | 1·56 | .... | 5·05 | .... | 0·62 |
| $Fe^2O^3$ | 0·70 | .... | 0·33 | FeO.... | 1·70 | $Mn^2O^3$ | 3·16 |
| $Al^2O^3$ | 35·12 | .... | 33·84 | .... | 35·45 | .... | 34·82 |
| $SiO^2$ | 44·12 | .... | 44·98 | .... | 45·80 | .... | 43·21 |
| HO | | .... | | .... | | .... | 2·04 |
| | 100·04 | ... | 99·66 | .... | 98·15 | .... | 99·45 |

6. *Praseolite.*—Rounded four, six, eight, and twelve-sided prisms, of specific gravity 2·754; harder than calcspar. Green. Gives off water when heated. Fuses with difficulty at the edges to a bluish green glass. (Erdmann.) If the protoxide of iron found by Erdmann may be estimated as sesquioxide, the formula will be : $MgO, SiO^2 + Al^2O^3, SiO^2 + Aq.$, one-sixth of the alumina, however, being replaced by sesquioxide of iron.

7. *Thomsonite, Comptonite.*—$NaO, SiO^2 + 3(CaO, SiO^2) + 4(Al^2O^3, SiO^2) + 8$ Aq. — *Thomsonite.* — Crystalline system, the square prismatic. Square prisms, with the lateral and terminal edges and the corners truncated. Specific gravity = 2·37. Harder than fluorspar. Transparent. Swells up before the blowpipe, becoming opaque, and fusing at the edges to a white enamel. With acids it yields a jelly.—*Comptonite.*—Belongs to the right prismatic system: *Fig.* 65 with *m*-faces; $i : i = 177° 35'$; $u^1 : u = 93° 45'$; cleavage parallel to *m*, *t*, and *u*. Harder than felspar. Transparent and colourless. Froths up before the blowpipe. When digested in the state of powder with nitric acid it yields a jelly.

| | | | *Thomsonite.* | | | Berzelius. Dumbarton. |
|---|---|---|---|---|---|---|
| KO | | .... | | | .... | |
| NaO | 1 | .... | 31·2 | 4·87 | .... | 4·53 |
| CaO | 3 | .... | 84·0 | 13·11 | .... | 13·54 |
| $Al^2O^3$ | 4 | .... | 205·6 | 32·08 | .... | 30·70 |
| $SiO^2$ | 8 | .... | 248·0 | 38·70 | .... | 38·30 |
| HO | 8 | .... | 72·0 | 11·24 | .... | 13·10 |
| | 1 | .... | 640·8 | 100·00 | .... | 100·17 |

*Comptonite.*

| | Rammelsberg. Seeberg. | Zippe. | Melly. Elbogen. |
|---|---|---|---|
| KO | 0·54 | .... | |
| NaO | 3·85 | 6·53 | 6·25 |
| CaO | 13·43 | 11·96 | 12·60 |
| $Al^2O^3$ | 30·84 | 32·00 | 31·07 |
| $SiO^2$ | 38·74 | 38·25 | 37·00 |
| HO | 13·10 | 11·50 | 12·24 |
| | 100·50 | 100·24 | 99·16 |

β. $2MO, 2Al^2O^3, 5SiO^2 = 2(MO, SiO^2) + 2Al^2O^3, 3SiO^2$.

1. *Iolite, Dichroite, Cordierite, Steinheilite, Peliome, Luchs-sapphire.*—Crystalline system, the square prismatic. *Fig.* 70; $u' : u = 120°$ nearly; cleavage imperfect, parallel to *p* and *u*. Specific gravity = 2·58; softer than quartz. Parallel to its axis it exhibits a blue colour, but perpendicular to it, a yellowish grey. Before the blowpipe it fuses with difficulty at the edges to a transparent stone-coloured glass. Dissolves with difficulty in borax and phosphate of soda, in the latter with separation of a skeleton of silica. It is but slightly attacked by acids. $3(MgO,SiO^2) + FeO, SiO^2 + 2(2Al^2O^3, 3SiO^2.)$ *Vid.* I., 93.

| | At. | *Iolite.* | | Stromeyer. Simiutak. | Bodenmais. |
|---|---|---|---|---|---|
| MgO | 3 | 60·0 | 9·83 | 11·45 | 10·16 |
| FeO | 1 | 35·2 | 5·76 | 4·34 | 8·32 |
| MnO | | | | 0·04 | 0·33 |
| $Al^2O^3$ | 4 | 205·6 | 33·66 | 33·12 | 31·71 |
| $SiO^2$ | 10 | 310·0 | 50·75 | 49·17 | 48·35 |
| HO | | | | 1·20 | 0·59 |
| | 1 | 610·8 | 100·00 | 99·32 | 99·46 |

| | Bonsdorff. Orrijerfvi. | Scheerer. *Cordierite.* | *Aspasiolite.* |
|---|---|---|---|
| MgO | 10·45 | 12·76 | 8·01 |
| FeO | 5·00 | 0·96 | 2·34 |
| MnO | 0·03 | trace | trace |
| $Al^2O^3$ | 32·88 | 32·95 | 32·38 |
| $SiO^2$ | 49·95 | 50·44 | 50·40 |
| HO | 1·75 | 1·02 | 6·73 |
| CaO | | 1·12 | trace |
| | 100·06 | 99·25 | 99·86 |

2. *Barsowite.*—Hard; sometimes granular and of specific gravity 2·751; sometimes compact, and of specific gravity 2·74. White and translucent. Before the blowpipe it fuses with difficulty at the edges only, and with slight evolution of gas bubbles, forming a blistered glass; with borax it yields a transparent glass, and also with phosphate of soda; in the latter case, the bead becomes opalescent on cooling, and contains an infusible skeleton of silica; with an equal proportion of carbonate of soda it yields a blistered glass; with a smaller quantity, a white infusible mass. In the state of powder, it is decomposed by hot hydrochloric acid and converted into a thick jelly. (G. Rose, *Pogg.* 48, 567.)

| | At. | | Varrentrapp. |
|---|---|---|---|
| CaO | 7 | 196·0 | 15·30 |
| MgO | 1 | 20·0 | 1·42 |
| $Al^2O^3$ | 8 | 411·2 | 33·78 |
| $SiO^2$ | 20 | 620·0 | 49·05 |
| | 1 | 1247·2 | 100·00 | 99·55 |

3. *Esmarkite.*—$2MgO, 2Al^2O^3, 5SiO^2, 2Aq.$—Large rounded prisms; cleavage parallel to the terminal face. Specific gravity = 2·709; hardness between calcspar and fluorspar. When heated it evolves water. Fuses before the blowpipe to a grey glass at the edges; dissolves in borax and in microcosmic salt, forming glasses which are coloured by iron; with carbonate of soda it forms a yellow slag. (Erdmann.)

| | At. | | *Esmarkite.* | | | Erdmann. |
|---|---|---|---|---|---|---|
| MgO | 10 | .... | 200·0 | 10·39 | .... | 10·32 |
| MnO | | .... | | | .... | 0·41 |
| FeO | 2 | .... | 70·4 | 3·65 | .... | 3·83 |
| $Al^2O^3$ | 12 | .... | 616·8 | 32·04 | .... | 32·08 |
| $SiO^2$ | 30 | .... | 930·0 | 48·31 | .... | 45·97 |
| HO | 12 | .... | 108·0 | 5·61 | .... | 5·49 |
| CaO, PbO, CoO, CuO, $TiO^2$ | | .... | | | .... | 0·45 |
| | 1 | .... | 1925·2 | 100·00 | .... | 98·55 |

4. *Fahlunite.*—$2(KO; CaO; MgO; MnO; FeO), 2Al^2O^3, 5SiO^2, 3Aq.$—Black crystals of the form of topaz and of specific gravity 2·74. Before the blowpipe it becomes colourless, cracks, and swells up slightly, fusing at the edges to a glass; assumes a blue colour when ignited with solution of cobalt; with borax or microcosmic salt, it yields a glass which is coloured by iron. (Wachtmeister.)

| | | | | | | Wachtmeister. | | |
|---|---|---|---|---|---|---|---|---|
| | At. | | *Fahlunite.* | | | Terra nova mine. | | Louisen mine. |
| KO | 1 | .... | 47·2 | 1·55 | .... | 1·98 | .... | 1·38 |
| CaO | 2 | .... | 56·0 | 1·84 | .... | 1·35 | .... | 0·95 |
| MgO | 10 | .... | 200·0 | 6·57 | .... | 6·75 | .... | 6·04 |
| MnO | 2 | .... | 71·2 | 2·34 | .... | 2·24 | .... | 1·90 |
| FeO | 3 | .... | 105·6 | 3·47 | .... | 3·86 | .... | 7·22 |
| $Al^2O^3$ | 18 | .... | 925·2 | 30·40 | .... | 30·10 | .... | 30·70 |
| $SiO^2$ | 45 | .... | 1395·0 | 45·84 | .... | 44·60 | .... | 44·95 |
| HO | 27 | .... | 243·0 | 7·99 | .... | 9·35 | .... | 8·65 |
| $SiF^2$ | | .... | | | .... | trace | .... | trace |
| | 1 | .... | 3043·2 | 100·00 | .... | 100·23 | .... | 101·79 |

5. *Brevicite.*—$2(NaO, CaO), 2Al^2O^3, 5SiO^2, 4Aq.$—Colourless prisms and laminar radiated masses.

| | | | | | | Sonden. |
|---|---|---|---|---|---|---|
| | At. | | *Brevicite.* | | | Strömi. |
| NaO | 8 | .... | 249·6 | 10·09 | .... | 10·32 |
| CaO | 6 | .... | 168·0 | 6·79 | .... | 6·88 |
| MgO | | .... | | | .... | 0·21 |
| $Al^2O^3$ | 14 | .... | 719·6 | 29.08 | .... | 28·39 |
| $SiO^2$ | 35 | .... | 1085·0 | 43·85 | .... | 43·88 |
| HO | 28 | .... | 252·0 | 10·19 | .... | 9·63 |
| | 1 | .... | 2474·2 | 100·00 | .... | 99·31 |

6. *Hydrated Iolite.*—$2(MgO; FeO), 2Al^2O^3, 5SiO^2, 4Aq.$—Regular six-sided prisms with truncated lateral edges; cleavage parallel to *p*. Rather harder than calcspar. Greenish brown and translucent. When heated it yields water and loses lustre, but suffers no further change. Before the blowpipe it becomes paler but does not fuse. It is not completely decomposed by acids. (Bonsdorff.)

| | At. | | | | Bonsdorff. |
|---|---|---|---|---|---|
| MgO | 3 | .... | 60·0 | 8·79 | 9·00 |
| FeO | 1 | .... | 35·2 | 5·16 | 5·30 |
| $Al^2O^3$ | 4 | .... | 205·6 | 30·11 | 30·05 |
| $SiO^2$ | 10 | .... | 310·0 | 45·40 | 45·05 |
| HO | 8 | .... | 72·0 | 10·54 | 10·60 |
| | 1 | .... | 682·8 | 100·00 | 100·00 |

7. *Mesole.*—That found at Faroe must be regarded as: $2(NaO; CO), 2Al^2O^3, 5SiO^2, 5Aq.$ That of Annaklef—though with less certainty—as: $1NaO, 1CaO, 2Al^2O^3, 5SiO^2, 4Aq.$; probably allied to Brevicite. The mineral yields a jelly with hydrochloric acid.

| | At. | | *Mesole.* | | Berzelius. Faroe. | | Hisinger. Annaklef. |
|---|---|---|---|---|---|---|---|
| NaO | 2 | .... | 62·4 | 5·76 | 5·63 | .... | 10·81 |
| CaO | 4 | .... | 112·0 | 10·34 | 11·43 | .... | 8·07 |
| $Al^2O^3$ | 6 | .... | 308·4 | 28·48 | 28·00 | .... | 26·80 |
| $SiO^2$ | 15 | .... | 465·0 | 42·95 | 42·60 | .... | 41·52 |
| HO | 15 | .... | 135·0 | 12·47 | 12·70 | .... | 11·79 |
| | 1 | .... | 1082·8 | 100·00 | 100·36 | .... | 98·99 |

### γ. $MO, Al^2O^3, 3SiO^2 = MO, SiO^2 + Al^2O^3, 2SiO^2.$

1. *Ryacolite.*—(Occurs in two forms, one portion resembling vitrefied felspar, another the ordinary variety of that mineral.)—$1(KO; NaO; CaO), 1Al^2O^3, 3SiO^2 = (KO; NaO; CaO), SiO^2 + Al^2O^3, 2SiO^2$.—Crystalline system, the oblique prismatic; $u' : u = 119° 21'$; $i : t = 90°$; cleavage parallel to $i$ and $t$. Specific gravity = 2·618. Before the blowpipe it fuses rather more readily than adularia, and at the same time imparts a more intense yellow colour to the flame. Hydrochloric acid decomposes it imperfectly, and separates pulverulent silica.

| | At. | | *Ryacolite.* | | G. Rose. Vesuvius. |
|---|---|---|---|---|---|
| KO | 3 | .... | 141·6 | 6·58 | 5·92 |
| NaO | 8 | .... | 249·6 | 11·60 | 10·56 |
| CaO | 1 | .... | 28·0 | 1·30 | 1·07 |
| MgO | | .... | | | 0·23 |
| $Fe^2O^3$ | | .... | | | 0·28 |
| $Al^2O^3$ | 12 | .... | 616·8 | 28·66 | 29·44 |
| $SiO^2$ | 36 | .... | 1116·0 | 51·86 | 50·31 |
| | 1 | .... | 2152·0 | 100·00 | 97·81 |

2. *Labrador.*—$1(NaO; CaO), 1Al^2O^3, 3SiO^2$, or: $NaO, SiO^2 + 3(CaO, SiO^2) + 4(Al^2O^3, 2SiO^2)$. —Crystalline system, the doubly oblique prismatic; cleavage in two directions which cross each other at an angle of about 93° 30′. Specific gravity, varying from 2·69 to 2·75. Resembles felspar, and behaves like that mineral before the blowpipe; fuses, however, at a somewhat lower temperature. Labrador is completely decomposed by concentrated hydrochloric acid.

| | At. | | *Labrador.* | | | Abich. Etna. | | Segeth. Radomisl. | | Le Hunte. Milngavia. |
|---|---|---|---|---|---|---|---|---|---|---|
| KO | | .... | | | .... | 0·22 | .... | 0·22 | .... | |
| NaO | 1 | .... | 31·2 | 4·50 | .... | 4·10 | .... | 3·64 | .... | 3·97 |
| CaO | 3 | .... | 84·0 | 12·13 | .... | 9·49 | .... | 10·63 | .... | 12·10 |
| MgO | | .... | | | .... | 1·74 | .... | | .... | |
| MnO | | .... | | | .... | 0·89 | .... | trace | .... | |
| $Fe^2O^3$ | | .... | | | .... | 1·60 | .... | 2·34 | .... | 0·30 |
| $Al^2O^3$ | 4 | .... | 205·6 | 29·68 | .... | 26·46 | .... | 27·19 | .... | 29·97 |
| $SiO^2$ | 12 | .... | 372·0 | 53·69 | .... | 53·48 | .... | 55·35 | .... | 52·34 |
| HO | | .... | | | .... | 0·42 | .... | 0·49 | .... | 0·87 |
| | 1 | .... | 692·8 | 100·00 | .... | 98·40 | .... | 99·86 | .... | 99·55 |

To this class also belong—so far at least as their composition is concerned—the minerals *Glaucolite* and *Ekebergite.*—*Glaucolite:* specific gravity=2·721. Softer than felspar. Blue and translucent. Fuses with difficulty; dissolves slowly in borax and microcosmic salt. (Bergemann.) —*Ekebergite,* on account of its mineralogical similarity, is generally classed with Mejonite and Wernerite; but the following analyses do not agree with this classification. The mineral exhibits a well marked plane of cleavage. It is harder than Wernerite. Specific gravity = 2·746. Transparent. Before the blowpipe it behaves like Wernerite.

| | *Glaucolite.* Bergemann. Baikal. | *Ekebergite.* Nordenskiold. Ersby. | Hartwell & Hedberg. Ersby. | Petteby. |
|---|---|---|---|---|
| KO | 1·27 | | | |
| NaO | 2·97 | | 3·86 | 5·12 |
| CaO | 10·27 | 15·46 | 13·53 | 9·33 |
| MgO | 3·73 | | | |
| FeO | 0·10 | | 0·55 | 1·91 |
| MnO | 0·87 | | | |
| $Al^2O^3$ | 27·60 | 29·23 | 27·60 | 32·27 |
| $SiO^2$ | 50·58 | 54·13 | 52·11 | 51·34 |
| HO | 1·73 | 1·07 | 0·73 | 1·00 |
| | 99·12 | 99·89 | 98·38 | 100·97 |

3. *Pinite.*—$KO,SiO^2+FeO,SiO^2+2(Al^2O^3,2SiO^2)+Aq.$?$=(KO;FeO)$, $SiO^2+Al^2O^3,2SiO^2$.—Crystalline system, the hexagonal. *Fig.* 135 and 139 (without the secondary face between *p* and *s*). $p : r = 138° 11'$. (Hauy.) Cleavage parallel to *p* and also parallel to *s*, though less distinct. Specific gravity = 2·78. Softer than felspar. Slightly translucent. It becomes colourless before the blowpipe, and fuses at the edges to a blistered glass, which is colourless, or—when a large proportion of iron is present—black. Dissolves in borax with difficulty, yielding a transparent glass; and with still greater difficulty in microcosmic salt, forming a glass which contains an insoluble skeleton of silica and becomes opalescent on cooling. (Berzelius.) It is but imperfectly decomposed by hydrochloric acid.—The want of accordance in the analyses renders it impossible to construct a formula which shall include the whole. Probably the water is not an essential constituent of the mineral.

| | At. | *Pinite.* | | Scott. Penig. | C. Gmelin. Auvergne. | Ficinus. Neustadt. |
|---|---|---|---|---|---|---|
| KO | 1 | 47·2 | 12·42 | 11·35 | 7·89 | 11·2 |
| NaO | | | | | 0·39 | |
| CaO | | | | 0·75 | | $Mn^2O^3$ 1·6 |
| MgO | | | | | 3·76 | 0·8 |
| FeO | 1 | 35·2 | 9·26 | 9·66 | 5·51 | 7·8 |
| $Al^2O^3$ | 2 | 102·8 | 27·04 | 28·00 | 25·48 | 23·6 |
| $SiO^2$ | 6 | 186·0 | 48·92 | 48·00 | 55·96 | 54·6 |
| HO | 1 | 9·0 | 2·36 | 3·00 | 1·41 | 1·2 |
| | 1 | 380·2 | 100·00 | 100·76 | 100·40 | 100·8 |

4. *Sodalite, Soda-Mesotype.*—$NaO,SiO^2+Al^2O^3,2SiO^2+2Aq.$—Belongs to the right prismatic system. *Fig.* 71, without the *y* face. $u' : u = 93° 22'$ (91° 20′. Phillips); $a : u = 116° 32'$; $a' : a = 144° 16'$; $t : u' = 133° 14'$; cleavage parallel to *u*. (Hauy.) According to G. Rose (*Pogg.* 28, 424) it belongs to the oblique prismatic system: for the angle between *u* and the *a* above, is 116° 27′, while that between *u* and the *a* below is only 115° 24′; $u' : u = 91° 35'$. Specific gravity from 2·17 to 2·25.

In hardness it is between fluorspar and felspar. Before the blowpipe it becomes turbid and then fuses tranquilly to a transparent glass. It dissolves readily in hydrochloric acid forming a siliceous jelly. According to Fuchs, it dissolves easily and without residue in oxalic acid, provided it does not contain scolezite mechanically combined.

| | At. | *Sodalite.* | | Smithson. Auvergne. | Fuchs. Auvergne. | | Fuchs. Högau. | | Von Kobell. Greenland. | |
|---|---|---|---|---|---|---|---|---|---|---|
| NaO | 1 | 31·2 | 16·12 | 17·0 | 16·12 | | 16·12 | | 14·70 | |
| CaO | | | | | 0·17 | | | | 1·80 | |
| $Fe^2O^3$ | | | | | | | 1·35 | | | |
| $Al^2O^3$ | 1 | 51·4 | 26·55 | 27·0 | 26·51 | | 25·60 | | 27·00 | |
| $SiO^2$ | 3 | 93·0 | 48·04 | 49·0 | 48·17 | | 47·21 | | 46·94 | |
| HO | 2 | 18·0 | 9·29 | 9·5 | 9·13 | | 8·88 | | 9·60 | |
| | 1 | 193·6 | 100·00 | 102·5 | 100·10 | | 99·16 | | 100·04 | |

5. *Scolezite, Calcareous Mesotype.*— $CaO, SiO^2 + Al^2O^3, 2SiO^2 + 3Aq.$, or, according to Kane: $CaO, HO, SiO^2 + Al^2O^3, 2SiO^2 + 2Aq$. For, as scolezite is isomorphous with sodalite, the CaO, HO in scolezite replaces the NaO in natrolite.—Crystalline form, the same as that of sodalite. Specific gravity = 2·21. Before the blowpipe it curls up in a vermicular shape, and then fuses easily to a blistered glass. With hydrochloric acid it behaves like sodalite; dissolves in oxalic acid with separation of oxalate of lime.

| | At. | *Scolezite.* | | Iceland. | Fuchs & Gehlen. Faroe. | | Staffa. |
|---|---|---|---|---|---|---|---|
| NaO | | | | | 0·48 | | 0·39 |
| CaO | 1 | 28·0 | 14·04 | 10·44 | 13·86 | | 14·20 |
| $Al^2O^3$ | 1 | 51·4 | 25·78 | 25·99 | 25·88 | | 24·82 |
| $SiO^2$ | 3 | 93·0 | 46·64 | 48·94 | 46·19 | | 46·75 |
| HO | 3 | 27·0 | 13·54 | 13·90 | 13·62 | | 13·64 |
| | 1 | 199·4 | 100·00 | 99·37 | 100·03 | | 99·80 |

6. *Mesolite.*—A mixture of one atom of sodalite and two atoms of scolezite. $1(NaO, Al^2O^3, 3SiO^3, 2Aq.) + 2(CaO, Al^2O^3, 3SiO^3, 3Aq.) = 1NaO, 2CaO, 3Al^2O^3, 9SiO^2, 8Aq.$

| | At. | *Mesolite.* | | Berzelius. Faroe. | Fuchs & Gehlen. Faroe. | Iceland. | Tyrol. |
|---|---|---|---|---|---|---|---|
| NaO | 1 | 31·2 | 5·27 | 5·40 | 5·47 | 4·79 | 5·20 |
| CaO | 2 | 56·0 | 9·45 | 9·87 | 9·35 | 10·06 | 9·61 |
| $Al^2O^3$ | 3 | 154·2 | 26·03 | 26·50 | 26·13 | 25·66 | 27·00 |
| $SiO^2$ | 9 | 279·0 | 47·10 | 46·80 | 47·00 | 46·78 | 46·04 |
| HO | 8 | 72·0 | 12·15 | 12·30 | 12·25 | 12·31 | 12·36 |
| | 1 | 592·4 | 100·00 | 100·87 | 100·20 | 99·60 | 100·21 |

### 3. $MO, Al^2O^3, 4SiO^2 = MO, SiO^2 + Al^2O^3, 3SiO^2$.

1. *Leucite.*—$KO, Al^2O^3, 4SiO^2 = KO, SiO^2 + Al^2O^3, 3SiO^2$. Belongs to the regular system. *Fig.* 11. Specific gravity from 2·4 to 2·5. In hardness it is between apatite and felspar; fracture conchoidal. Transparent. Infusible before the blowpipe; dissolves with difficulty though abundantly in borax, yielding a transparent glass; scarcely soluble in microcosmic salt; effervesces with carbonate of soda, and fuses with difficulty to a clear blistered glass. (Berzelius.) When treated in a finely divided state with hydrochloric acid, it is completely decomposed, with separation of pulverulent silica,

| | At. | *Leucite.* | | Klaproth. | Arfvedson. | Awdejew. |
|---|---|---|---|---|---|---|
| KO..... | 1 | 47·2 | 21·20 | 22 | 21·15 | 20·40 |
| NaO ... | ... | ... | ... | ... | ... | 1·02 |
| $Fe^2O^3$... | ... | ... | ... | ... | 0·95 | ... |
| $Al^2O^3$... | 1 | 51·4 | 23·09 | 23 | 23·10 | 23·03 |
| $SiO^2$ ... | 4 | 124·0 | 55·71 | 54 | 56·10 | 56·05 |
| | 1 | 222·6 | 100·00 | 99 | 101·30 | 100·50 |

When solution of silica is added to an aqueous solution of alumina in potash, the mixture solidifies after a few minutes to a semi-opaque jelly, in consequence of the separation of a double silicate of alumina and potash, which, according to Berzelius, has the same composition as leucite; the excess of potash remains dissolved in the liquid.

2. *Andesine.*—1(KO; NaO; CaO; MgO), $1Al^2O^3$, $4SiO^2$=(KO; NaO; CaO; MgO), $SiO^2+Al^2O^3$, $3SiO^2$.—Belongs to the doubly oblique prismatic system. Specific gravity = 2·733. Resembles felspar. Fuses much more readily than albite, and yields a turbid glass. (Abich.)

| | At. | *Andesine.* | | Abich. Marmoto. |
|---|---|---|---|---|
| KO ..... | 1 | 47·2 | 1·00 | 1·08 |
| NaO..... | 10 | 312·0 | 6·58 | 6·53 |
| CaO..... | 10 | 280·0 | 5·91 | 5·77 |
| MgO ..... | 2 | 40·0 | 0·84 | 1·08 |
| $Fe^2O^3$ ..... | 1 | 78·4 | 1·65 | 1·58 |
| $Al^2O^3$ ..... | 22 | 1130·8 | 23·86 | 24·28 |
| $SiO^2$..... | 92 | 2852·0 | 60·16 | 59·60 |
| | 1 | 4740·4 | 100·00 | 99·92 |

3. *Analcime.*—$1NaO, 1Al^2O^3, 4SiO^2, 2Aq. = NaO, SiO^2 + Al^2O^3, 3SiO, + 2Aq.$—Belongs to the regular system. Primary form a cube; occurs also in octohedrons like those of leucite, and in cubes, often with the faces of the leucite-octohedron replacing the edges. Cleavage indistinct parallel to the faces of the cube. Specific gravity from 2·1 to 2·2. Softer than felspar. Transparent, and colourless.—Before the blowpipe it loses water and becomes milk-white; but when the heat is increased it again becomes clear, and then fuses quietly to a transparent glass. It is readily decomposed by hydrochloric acid, with separation of viscid silica; after ignition, however, the decomposition becomes more difficult.

| | At. | *Analcime.* | | H. Rose. Fassa. | Connell. Kilpatrik. | Awdejew. Brevig. |
|---|---|---|---|---|---|---|
| NaO..... | 1 | 31·2 | 13·89 | 13·53 | 13·71 | 14·23 |
| $Al^2O^3$ ..... | 1 | 51·4 | 22·89 | 22·99 | 22·23 | 23·55 |
| $SiO^2$..... | 4 | 124·0 | 55·21 | 55·12 | 55·07 | 55·16 |
| HO ..... | 2 | 18·0 | 8·01 | 8·27 | 8·22 | 8·26 |
| | 1 | 224·6 | 100·00 | 99·91 | 99·23 | 101·20 |

4. *Ledererite.*—$1CaO, 1Al^2O^3, 4SiO^2, 2Aq = CaO, SiO^2 + Al^2O^3, 3SiO^2 + 2Aq.$; one third of the lime is, however, replaced by soda. Phosphate of lime is also present, but whether it is essential to the composition of the mineral has not yet been determined.—Crystalline system, the hexagonal (B, *a*, I., 16). *Fig.* 137, $p : r = 130$. Specific gravity = 2·169; of the same degree of hardness as felspar. Transparent and colourless. (Jackson.) Before the blowpipe it becomes opaque, and subsequently yields a white enamel, which, by long continued exposure to the flame,

becomes more glassy. Effervesces with carbonate of soda, and yields a white enamel. Perfectly decomposed by hydrochloric acid. (Hayes, *Sil. Amer. J.* 25, 78.)

| | At. | *Ledererite.* | | Hayes. | from Cape Blomidon. Without $3CaO, PO^5$ |
|---|---|---|---|---|---|
| NaO | 1 | 31·2 | 4·67 | 3·94 | 4·33 |
| CaO | 2 | 56·0 | 8·39 | 7·38 | 8·10 |
| $Fe^2O^3$ | | | | 0·14 | 0·15 |
| $Al^2O^3$ | 3 | 154·2 | 23·10 | 21·48 | 23·60 |
| $SiO^2$ | 12 | 372·0 | 55·75 | 49·47 | 54·37 |
| HO | 6 | 54·0 | 8·09 | 8·58 | 9·44 |
| $3CaO, PO^5$ | | | | 7·58 | |
| | 1 | 667·4 | 100·00 | 98·57 | 99·99 |

5. *Caporcianite?*—$1CaO, 1Al^2O^3, 4SiO^2, 3Aq$.—Swells up slightly before the blowpipe, and fuses immediately afterwards. (Anderson, *N. Edinb. Phil. J.* 34, 21.) [This mineral is probably related to Lomonite.]

| | At. | *Caporcianite.* | | Anderson. |
|---|---|---|---|---|
| KO | | | | 1·1 |
| NaO | | | | 0·2 |
| CaO | 1 | 28·0 | 12·15 | 11·3 |
| MgO | | | | 0·4 |
| $Fe^2O^3$ | | | | 0·1 |
| $Al^2O^3$ | 1 | 51·4 | 22·31 | 21·7 |
| $SiO^2$ | 4 | 124·0 | 53·82 | 52·8 |
| HO | 3 | 27·0 | 11·72 | 13·1 |
| | 1 | 230·4 | 100·00 | 100·7 |

6. *Lomonite.*—$1CaO, 1Al^2O^3, 4SiO^2, 4Aq. = CaO, SiO^2 + 1Al^2O^3 3SiO^2 + Aq$.—Belongs, according to Hauy, to the right prismatic system; *Fig.* 65 with the *m*-face; $u' : u = 98° 12'$; $i : t = 121° 29'$. According to Phillips, it belongs to the oblique prismatic system; primary form: *Fig.* 81; $i : u'$ or $u = 86° 15'$; $u' := 113° 30'$. Specific gravity $= 2·3$. Softer than calcspar. Transparent and colourless. When exposed to the air, it swells up slowly and forms an opaque friable mass. Before the blowpipe this change takes place immediately; after which, the mineral yields a white enamel, which, at a higher temperature, becomes transparent. Dissolves with ease in hydrochloric acid, a siliceous jelly being separated.

| | At. | *Lomonite.* | | Dufrenoy. Phillipsburg. | Connell. Suizort. |
|---|---|---|---|---|---|
| CaO | 1 | 28·0 | 11·28 | 11·71 | 10·62 |
| $Al^2O^3$ | 1 | 51·4 | 21·47 | 21·12 | 21·14 |
| $SiO^2$ | 4 | 124·0 | 51·80 | 51·98 | 52·04 |
| HO | 4 | 36·0 | 15·45 | 15·05 | 14·92 |
| | 1 | 239·4 | 100·00 | 99·86 | 98·72 |

7. *Chabasite.*—$1(KO; NaO; CaO), 1Al^2O^3, 4SiO^2, 6Aq = (KO; NaO; CaO), SiO^2 + Al^2O^3, 3SiO^2 + 6Aq$.—The variety richer in lime is called *Ordinary* or *Calcareous Chabasite;* that which is richer in soda, *Gmelenite, Spurious Sarcolite, Hydrolite,* or *Soda-chabasite.*—Crystalline system, the rhombohedral; primary form an obtuse rhombohedron: *Fig.* 141 and 143 with a *a*-face; $r^3 : r^5 = 93° 48'$; $r^1 : r^3 = 86° 12'$; cleavage imperfect parallel to *r*. (Hauy.) Specific gravity, from 2·0 to 2·1. Softer than felspar. Transparent and colourless. Shrinks up before the blowpipe

and fuses to a blistered, slightly translucent enamel. It is perfectly decomposed when treated in the state of powder by hydrochloric acid;—calcareous chabasite is decomposed with comparative difficulty and separation of viscid silica; soda-chabasite more readily, with formation of siliceous jelly.

| | At. | | *Soda-Chabasite.* | | Rammelsberg. Glenarm. | Connell. |
|---|---|---|---|---|---|---|
| KO | | | | | 1·73 | 0·39 |
| NaO | 2 | | 62·4 | 8·02 | 7·20 | 3·85 |
| CaO | 1 | | 28·0 | 3·59 | 3·78 | 6·13 |
| $Fe^2O^3$ | | | | | | 0·11 |
| $Al^2O^3$ | 3 | | 154·2 | 19·80 | 20·63 | 18·05 |
| $SiO^2$ | 12 | | 372·0 | 47·78 | 46·48 | 48·56 |
| HO | 18 | | 162·0 | 20·81 | 20·41 | 21·66 |
| | 1 | | 778·6 | 100·00 | 100·23 | 98·75 |

| | At. | | *Calcareous Chabasite.* | | Berzelius. Faroe. | Hoffman. Aussig. | Fassa. |
|---|---|---|---|---|---|---|---|
| KO | | | | | 0·41 | 0·21 | 0·28 |
| NaO | 1 | | 31·2 | 3·02 | 2·75 | 1·54 | 0·56 |
| CaO | 3 | | 84·0 | 8·13 | 8·35 | 9·65 | 10·22 |
| MgO | | | | | 0·40 | | |
| $Al^2O^3$ | 4 | | 205·6 | 19·91 | 20·00 | 19·27 | 19·52 |
| $SiO^2$ | 16 | | 496·0 | 48·03 | 48·00 | 48·18 | 48·63 |
| HO | 24 | | 216·0 | 20·91 | 19·30 | 21·10 | 20·70 |
| | 1 | | 1032·8 | 100·00 | 99·21 | 99·95 | 99·91 |

Many varieties of calcareous chabasite appear to contain $4\frac{1}{2}$ atoms instead of 4 atoms of silica; this, however, is regarded by Berzelius as arising from an admixture of quartz. Whether *Levyne*, which, on the contrary contains less silica, is allied to calcareous chabasite, is still a matter of dispute. ¶ Genth (*Ann. Pharm.* 66, 270) finds in a variety of chabasite occurring at Annerode near Giessen, 47 per cent. $SiO^2$, 19·71 $Al^2O^3$, 0·15 $Fe^2O^3$, 10·63 CaO, 0·65 NaO, 0·33 KO, and 22·29 water. From this he deduces the formula, $3(CaO, NaO, KO)\,3Al^2O^3, 4SiO^2, 18Aq$. According to Engelhardt, 3 atoms of water out, of the 18, are driven off at 100°, and 12 atoms more at a higher temperature, the last 3 atoms being more intimately combined than the rest. ¶

ε. $MO, Al^2O^3, 6SiO^2 = MO, 3SiO^2 + Al^2O^3, 3SiO^2$.

1. *Felspar. Potash-felspar, Orthoclase.*—$KO, Al^2O^3, 6SiO^2 = KO, 3SiO^2 + Al^2O^3, 3SiO^2$.—Crystalline system, the oblique prismatic. *Fig.* 81, 82, and many other forms, namely those with $a$ and $f$-faces; $i : t = 90°$; $u' : u = 118° 48·6'$; $u : t = 120° 35·7'$; $a : a = 90° 6·9'$ (90°, G. Rose). (Kupffer.) Cleavage distinct, parallel to $i$ and $t$; indistinct, parallel to $u$; specific gravity from 2·496 to 2·601, and increasing in proportion as the potash is replaced by soda and lime. Softer than quartz, but harder than apatite; gives faint sparks with steel. Transparent and colourless. Fuses with great difficulty to a blistered, turbid glass. In borax it dissolves slowly, forming a transparent glass. In microcosmic salt it dissolves when reduced to powder, but with great difficulty and separation of a skeleton of silica, and yields a glass which becomes opalescent on cooling. With carbonate of soda it effervesces, and is slowly converted into a transparent, blistered, and very infusible glass; with solution of cobalt it assumes a blue colour at the fused edges only. (Berzelius.)

A mixture of equal weights of felspar and white marble, fused in a charcoal crucible in a blast-furnace, yields a transparent glass which is readily dissolved by acids, and contains only 5·9 parts of potash to 64·1 parts of silica; $\frac{2}{3}$ of the potash must therefore be volatilized. (Berthier.) Powdered felspar dissolves with difficulty and but partially in hot hydrochloric acid. (G. Rose.) If powdered felspar is gently ignited with lime and the mass then digested with water, or if powdered felspar previously ignited is boiled with milk of lime, it gives up its potash to the water, the lime taking the place of potash in the compound. (Fuchs, Zierl.) Felspar in a state of minute division is not sensibly acted upon by water at a temperature of 100°; at 125° (257° F.) in a Papin's digester it renders the water feebly alkaline; at 150° (302° F.) strongly; and at 220° (428° F.) still more strongly alkaline. The compound $KO,4SiO^2$ is probably dissolved out in this process, which is of the same nature as the slow efflorescence by which felspar is decomposed in nature: for when felspar = $KO,Al^2O^3,6SiO^2$ gives up $KO,4SiO^2$ to the water, there remains $Al^2O^3,2SiO^2$, which, with 2 atoms of water, constitutes clay. (Forchhammer, *Pogg.* 35, 353.)

| | At. | *Potash-Felspar.* | | Abich. *a.* | *b.* | G. Rose. *c.* |
|---|---|---|---|---|---|---|
| KO | 1 | 47·2 | 16·59 | 13·99 | 14·02 | 14·73 |
| NaO | | | | 1·01 | 1·25 | trace |
| CaO | | | | 1·34 | 0·34 | 0·60 |
| MgO | | | | | | |
| MnO | | | | | | |
| $Fe^2O^3$ | | | | trace | trace | |
| $Al^2O^3$ | 1 | 51·4 | 18·06 | 17·97 | 18·57 | 19·15 |
| $SiO^2$ | 6 | 186·0 | 65·35 | 65·69 | 65·72 | 65·52 |
| | 1 | 284·6 | 100·00 | 100·00 | 100·00 | 100·00 |

| | Abich. *d.* | *e.* | *f.* |
|---|---|---|---|
| KO | 9·12 | 8·27 | 6·68 |
| NaO | 3·49 | 4·10 | 2·86 |
| CaO | 1·23 | 1·23 | 3·16 |
| MgO | 1·03 | 1·20 | 1·40 |
| MnO | 0·13 | | |
| $Fe^2O^3$ | 0·83 | 0·81 | 2·41 |
| $Al^2O^3$ | 18·64 | 17·36 | 15·72 |
| $SiO^2$ | 65·00 | 66·73 | 67·87 |
| | 99·47 | 99·70 | 100·10 |

*a*, is Adularia, from St. Gotthard;—*b*, ordinary felspar, from Baveno, of specific gravity 2·555;—*c*, glassy felspar from Vesuvius;—*d*, the same variety from the lava of Arso, of specific gravity 2·6012;—*e*, a similar variety from Epomeo, of specific gravity 2·5972;—*f*, the same from the tuff of Pausilippo, of specific gravity 2·651. Hence, it appears that it is chiefly in the glassy felspars occurring in volcanic regions, that a portion of the potash is replaced by soda, lime, and magnesia. Breithaupt's *Valencianite* and *Microcline* have precisely the same composition as felspar.

*Artificial felspar*, with the same crystalline form and composition as the native mineral, has been found on the wall of a smelting furnace in which copper ore was reduced. (Kersten, Heine, *Pogg.* 33, 336; 34,431.) When felspar, or a mixture of its component parts, is fused, no crystals are obtained, even when the mass is cooled very slowly, but merely a glass. (Mitscherlich.)

2. *Albite, Soda-felspar.*—$1NaO, 1Al^2O^3, 6SiO^2 = NaO, 3SiO^2 + Al^2O^3, 3SiO^2$. When a portion of the soda is replaced by potash, the mineral is called *Pericline* and *Potash-albite*. Albite belongs to the doubly oblique system of crystallization. Primary form, *Fig.* 121, with the *z*-face replacing the acute angle between *u* and *v*; $y : u = 93° 36'$; $y : v = 115° 5'$; $u : v = 117° 55'$; $u : z = 119° 52'$; $v : z = 122° 15'$; cleavage parallel to *y*, *u*, and *v*, but most distinct parallel to *y*. It almost always occurs in macle-crystals. (G. Rose.) Specific gravity of albite = 2·614; of pericline = 2·641; of potash-albite = 2·622. (Abich.) It is very like felspar. Before the blowpipe albite behaves like felspar, imparting, however, a more distinct yellow colour to the flame. Pericline fuses more readily. Not decomposed by aqueous acids or alkalis.

| | At. | *Albite.* | | Eggertz. Finbo. | Stromeyer. Chesterfield. | G. Rose. Arendal. | Thaulow. St. Gotthard. |
|---|---|---|---|---|---|---|---|
| NaO | 1 | 31·2 | 11·62 | 10·50 | 9·06 | 9·12 | 11·47 |
| CaO | | | | 0·55 | 0·24 | 0·68 | |
| $Fe^2O^3$ | | | | | 0·11 | 0·28 | 0·20 |
| $Al^2O^3$ | 1 | 51·4 | 19·13 | 18·45 | 19·80 | 19·30 | 19·43 |
| $SiO^2$ | 6 | 186·0 | 69·25 | 70·48 | 70·68 | 68·46 | 69·00 |
| | 1 | 268·6 | 100·00 | 99·98 | 99·89 | 97·84 | 100·10 |

The albite analyzed by Thaulow was regarded as pericline. The *Pericline* of Zöblitz, analyzed by C. Gmelin, consists of about 1KO, 6NaO (total 7), $7Al^2O^3$, $42SiO^2$; and that from the island of Pentellaria analyzed by Abich, 2KO, 10NaO, 2CaO, 1MgO (total 15), $15Al^2O^3$, $90SiO^2$. —The *Potash-albite*, from the trachyte of the Drachenfels, is, 2KO, 5NaO, 2CaO (total 9), $9Al^2O^3$, $54SiO^2$.

3. *Epistilbite.*—$1CaO, 1Al^2O^3, 6SiO^2, 5Aq., = CaO, 3SiO^2 + Al^2O^3, 3SiO^2 + Aq.$—Crystalline system, the right prismatic. *Fig.* 64, without the *i*-face; $u' : u = 135° 10'$; $a : u = 96° 6'$. Cleavage distinct, parallel to the acute lateral edge (*t*-face). Specific gravity = 2·25. In hardness it is intermediate between felspar and apatite. Transparent and colourless. When heated, it swells up strongly and evolves water. Before the blowpipe it intumesces and yields a highly blistered enamel, which does not run into a globule. With borax and with microcosmic salt it yields a transparent glass, accompanied in the latter case with a skeleton of silica. With carbonate of soda it forms a clear blistered glass, and with solution of cobalt a blue enamel. It dissolves in concentrated hydrochloric acid, with separation of silica in the form of a granular powder; after ignition, however, it is perfectly insoluble. (G. Rose.)

| | At. | *Epistilbite.* | | G. Rose. |
|---|---|---|---|---|
| NaO | | | | 1·78 |
| CaO | 1 | 28·0 | 9·02 | 7·56 |
| $Al^2O^3$ | 1 | 51·4 | 16·56 | 17·52 |
| $SiO^2$ | 6 | 186·0 | 59·92 | 58·59 |
| HO | 5 | 45·0 | 14·50 | 14·48 |
| | 1 | 310·4 | 100·00 | 99·93 |

4. *Stilbite, Desmine.*—$1CaO, 1Al^2O^3, 6SiO^2, 6Aq. = CaO, 3SiO^2 + Al^2O^3, 3SiO^2 + 6Aq.$—Crystalline system, the right prismatic (or the oblique prismatic?) Right rectangular prisms with four-sided summits resting on the lateral edges; consequently with the *m*, *t*, *a*, and *p*-faces; $p : a = 133° 3'$; $a : m = 123° 53'$; $a : t = 118° 14'$; $a : a = 123° 32'$ and $112° 14'$. Cleavage very distinct parallel to *m*. Specific gravity = 2·16. As hard as fluorspar. Transparent and colourless, and with a

beautiful pearly lustre on the *m*-faces. Swells up strongly before the blowpipe and fuses with difficulty to a blistered glass. It is slowly but completely decomposed by concentrated hydrochloric acid, with separation of silica in the form of a viscid powder.

| | At. | | *Stilbite.* | | | Hisinger. Iceland. | | Mosa. Faroe. |
|---|---|---|---|---|---|---|---|---|
| KO | | .... | | | .... | | .... | 0·32 |
| NaO | | .... | | | .... | | .... | 1·11 |
| CaO | 1 | .... | 28·0 | 8·77 | .... | 9·20 | .... | 7·74 |
| $Al^2O^3$ | 1 | .... | 51·4 | 16·09 | .... | 16·10 | .... | 16·44 |
| $SiO^2$ | 6 | .... | 186·0 | 58·23 | .... | 58·00 | .... | 57·18 |
| HO | 6 | .... | 54·0 | 16·91 | .... | 16·40 | .... | 17·79 |
| | 1 | .... | 319·4 | 100·00 | .... | 99·70 | .... | 100·58 |

*i.* 3 *Atoms of stronger base with* 4 *atoms of Alumina.*

*α. Oligoclase, Soda-spodumene.* — $3NaO, 4Al^2O^3, 16SiO^2 = (3NaO, 4SiO^2) + 4(Al^2O^3, 3SiO^2)$. A portion of the soda is replaced by potash, lime, and magnesia. Crystalline system, the doubly oblique prismatic. Specific gravity = 2·668. Resembles felspar, but fuses with much greater facility to a transparent and colourless glass. Not decomposed by acids.

| | At. | | *Oligoclase.* | | | Berzelius. Ytterby. | | Laurent. Arriège. | | Hagen. Arendal. |
|---|---|---|---|---|---|---|---|---|---|---|
| KO | | .... | | | .... | 0·38 | .... | | .... | 2·19 |
| NaO | 3 | .... | 93·6 | 11·77 | .... | 9·67 | .... | 8·9 | .... | 9·37 |
| CaO | | .... | | | .... | 3·18 | .... | 3·0 | .... | 2·44 |
| MgO | | .... | | | .... | 0·80 | .... | 0·2 | .... | 0·77 |
| $Al^2O^3$ | 4 | .... | 205·6 | 25·86 | .... | 23·80 | .... | 24·6 | .... | 23·09 |
| $SiO^2$ | 16 | .... | 496·0 | 62·37 | .... | 61·55 | .... | 62·6 | .... | 63·51 |
| $Fe^2O^3$ | | .... | | | .... | | .... | 0·1 | .... | |
| | 1 | .... | 795·2 | 100·00 | .... | 99·38 | .... | 99·4 | .... | 101·37 |

Most of the analyses of this mineral, however, correspond more exactly to the formula, $4NaO, 5Al^2O^3, 21SiO^2$; some, as those of Rosales and Bodemann, likewise correspond to $1NaO, 1Al^2O^3, 5SiO^2$; but there is generally a deficiency in the quantity of the stronger base. Most probably the proportions are $3NaO, 4Al^2O^3, 15SiO^2$; because these proportions likewise occur in spodumene, and because the number of atoms of silica therein contained is exactly half that which occurs in petalite. Further analyses of specimens of oligoclase of the utmost possible purity, are necessary to decide the question.

*β. Spodumene, Triphane.*—Either $3LiO, 4Al^2O^3, 15SiO^2 = 3(LiO, SiO^2) + 4(Al^2O^3, 3SiO^2)$; or $3LiO, 4Al^2O^3, 16SiO^2 = 3LiO, 4SiO^2 + 4(Al^2O^3, 3SiO^2)$. A portion of the lithia is replaced by soda. Occurs in crystalline masses with two planes of cleavage, one more and one less distinct, and intersecting each other at an angle of 105°. Specific gravity = 3·2; harder than felspar. Swells up before the blowpipe, imparting at the same time a slight and transient purple-red colour to the flame, and fusing with tolerable facility to a nearly transparent glass. With solution of cobalt it gives a blue glass. When mixed in a finely divided state with fluorspar and bisulphate of potash, it imparts a brighter red colour to the blowpipe flame. It is not acted on by acids. Spodumene exposed in a charcoal crucible to the heat of a blast-furnace, yields a glass which

resists the action of acids; with an equal weight of carbonate of lime, it yields—without any loss of lithia by volatilization—a transparent glass which is perfectly decomposed by acids. (Berthier.)

| | At. | | *Spodumene.* | | Stromeyer. | | Regnault. | | Hagen. |
|---|---|---|---|---|---|---|---|---|---|
| NaO | | .... | | .... | | .... | | .... | 2·68 |
| LiO | 3 | .... | 43·2 | 6·05 | 5·63 | .... | 6·76 | .... | 3·84 |
| $Mn^2O^3$ | | .... | | .... | 0·20 | .... | | .... | |
| $Fe^2O^3$ | | .... | | .... | 0·79 | .... | 2·83 | .... | 0·32 |
| $Al^2O^3$ | 4 | .... | 205·6 | 28·80 | 28·78 | .... | 25·34 | .... | 27·02 |
| $SiO^2$ | 15 | .... | 465·0 | 65·15 | 63·29 | .... | 65·30 | .... | 66·14 |
| HO | | .... | | .... | 0·77 | .... | | .... | |
| | 1 | .... | 713·8 | 100·00 | 99·46 | .... | 100·23 | .... | 100·00 |

Assuming the formula to be: $3LiO, 4Al^2O^3, 16SiO^2$, calculation would give 5·8 per cent. of lithia, 27·6 of alumina, and 66·6 of silica.

γ. *Petalite.*—$1NaO, 2LiO, 4Al^2O^3, 30SiO^2 = NaO, 2SiO^2 + 2(LiO, 2SiO^2) + 4(Al^2O^3, 6SiO^2)$. Belongs apparently to the doubly oblique prismatic system. Presents two planes of cleavage, one more and one less distinct, and intersecting each other at an angle of 141½°. Specific gravity from 2·4 to 2·44. Rather harder than felspar. Resembles that mineral in external appearance; but fuses readily and tranquilly to a turbid and rather blistered glass, imparting at the same time a red colour to the blowpipe flame, especially when mixed in the state of powder with fluorspar and bisulphate of potash. Not decomposed either by hydrochloric or by sulphuric acid, even after ignition.

| | At. | | *Petalite.* | | Hagen. | | C. Gmelin. | | Arfvedson. |
|---|---|---|---|---|---|---|---|---|---|
| NaO | 1 | .... | 31·2 | 2·61 | 2·30 | .... | 5·16 | .... | 5·76 |
| LiO | 2 | .... | 28·8 | 2·41 | 2·69 | | | | |
| CaO | | .... | | .... | | .... | 0·32 | .... | |
| $Al^2O^3$ | 4 | .... | 205·6 | 17·19 | 17·20 | .... | 17·41 | .... | 17·22 |
| $SiO^2$ | 30 | .... | 930·0 | 77·79 | 77·81 | .... | 74·17 | .... | 79·21 |
| HO | | .... | | .... | | .... | 2·17 | .... | |
| | 1 | .... | 1195·6 | 100·00 | 100·00 | .... | 99·23 | .... | 102·19 |

¶ Breithaupt (*Pogg.* 69, 441) describes a mineral containing lithia which greatly resembles Stilbite or Heulandite in appearance. He has given it the name of *Zygadite*, from ζυγαδὸν (occurring in pairs). It is found near Zellerfeld in the Hartz, accompanied by quartz and very small rhombohedral crystals of chabasite. It has a vitreous lustre; the fractured surfaces, however, have a lustre between that of glass and that of mother-of-pearl; its colour is reddish and yellowish white; sometimes feebly translucent, but generally quite opaque or turbid. Primary form, a rhombic prism of about 136° and 44°; has a distinct plane of cleavage, and its fracture is uneven. Hardness from 7 to 7½, being somewhat greater than that of scapolite. Contains lithia, alumina, and silica; but the proportions have not been determined. Chemically, it is allied to Petalite and Castor. ¶

δ. *Gismondine, Zeagonite.*—$1KO, 2CaO, 4Al^2O^3, 11SiO^2, 15Aq. = KO, SiO^2 + 2(CaO, SiO^2) + 4(Al^2O^3, 2SiO^2) + 15Aq$. Resembles harmotome in the form of its crystals. Specific gravity = 2·18. Dissolves readily and completely in hydrochloric acid, yielding a siliceous jelly on evaporation.

| | At. | | *Gismondine.* | | Kobell. |
|---|---|---|---|---|---|
| KO | 1 | .... | 47·2 | 6·02 .... | 6·28 |
| CaO | 2 | .... | 56·0 | 7·13 .... | 7·60 |
| $Al^2O^3$ | 4 | .... | 205·6 | 26·20 .... | 25·77 |
| $SiO^2$ | 11 | .... | 341·0 | 43·45 .... | 42·72 |
| HO | 15 | .... | 135·0 | 17·20 .... | 17·66 |
| | 1 | .... | 784·8 | 100·00 .... | 100·03 |

ι. *Leonhardite.*—Crystalline system, the oblique prismatic. *Fig.* 91: $u : u^1 = 83° 30'$; $i : u = 114°$; cleavage distinct parallel to $u$; indistinct parallel to $i$. Translucent, white, and of a pearly lustre. Effloresces in the air. When heated, it evolves a considerable quantity of water, swells up and fuses with intumescence to a white enamel. With borax it forms a transparent glass. Dissolves readily in hydrochloric acid. (Blum, *Pseudomorphosen*, 104.)

| | At. | | *Leonhardite.* | | Delffs. |
|---|---|---|---|---|---|
| CaO | 3 | .... | 84·0 | 9·40 .... | 9·25 |
| $Al^2O^3$ | 4 | .... | 205·6 | 23·01 .... | 22·98 |
| $SiO^2$ | 16 | .... | 496·0 | 55·51 .... | 56·13 |
| HO | 12 | .... | 108·0 | 12·08 .... | 11·64 |
| | 1 | .... | 893·6 | 100·00 .... | 100·00 |

$(3CaO, 4SiO^2) + 4(Al^2O^3, 3SiO^2) + 12Aq.$

ζ. *Harmotome, Cross-stone.*—Crystalline system, the right prismatic. Rectangular prisms ($t$ and $m$ faces), with four-sided summits ($a$-faces), resting on the lateral edges; cleavage distinct, parallel to $t$ (the narrow lateral face); less distinct parallel to $m$; the crystals are generally inserted crossways into each other. Harder than fluorspar. Before the blowpipe it gives off water and fuses to a transparent glass.

1. *Potash-harmotome, Calcareous-harmotome,* or *Phillipsite.*—$1KO, 2CaO, 4Al^2O^3, 15SiO^2, 18Aq. = KO, SiO^2 + 2(CaO, SiO^2) + 4(Al^2O^3, 3SiO^2) + 18Aq.$ Specific gravity from 2·16 to 2·17. Loses water before the blowpipe, swells slightly, and then fuses to a translucent glass. It is easily and completely decomposed by hydrochloric acid, with separation of gelatinous silica.

| | At. | | *Potash-harmotome.* | | Wernekink. Annerode. | | L. Gmelin. Marburg. | | Köhler. Marburg. | | Cassel. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| KO | 1 | .... | 47·2 | 5·04 | .... 6·41 | .... | 6·33 | .... | 3·95 | .... | 3·89 |
| BaO | | .... | | | .... 0·46 | .... | | .... | | .... | |
| CaO | 2 | .... | 56·0 | 5·99 | .... 5·91 | .... | 6·26 | .... | 6·50 | .... | 7·22 |
| $Fe^2O^3$ | | .... | | | .... 0·41 | .... | 0·99 | .... | | .... | |
| $Al^2O^3$ | 4 | .... | 205·6 | 21·97 | .... 20·00 | .... | 21·76 | .... | 21·78 | .... | 23·33 |
| $SiO^2$ | 15 | .... | 465·0 | 49·69 | .... 48·36 | .... | 48·51 | .... | 50·44 | .... | 48·22 |
| HO | 18 | .... | 162·0 | 17·31 | .... 17·09 | .... | 17·23 | .... | 16·81 | .... | 17·56 |
| | 1 | .... | 935·8 | 100·00 | .... 98·64 | .... | 101·08 | .... | 99·48 | .... | 100·22 |

2. *Baryta-harmotome.*—$3BaO, 4Al^2O^3, 18SiO^2, 18Aq. = 3(BaO, 2SiO^2) + 4(Al^2O^3, 3SiO^2) + 18Aq.$ Specific gravity from 2·40 to 2·43. When finely pounded, it is perfectly decomposed by hydrochloric acid, though with difficulty, silica being separated in the pulverulent state.

| | At. | *Baryta-harmotome.* | | Rammelsberg. Andreasberg. | | Connell. Strontian. | | Köhler. Oberstein. |
|---|---|---|---|---|---|---|---|---|
| KO & NaO | .... | | .... | | .... | 1·72 | .... | 1·10 |
| BaO | 3 | 229·8 | 19·89 | .... | 19·22 | 20·85 | .... | 19·12 |
| CaO | .... | | .... | | .... | 0·10 | .... | |
| $Fe^2O^3$ | .... | | .... | | .... | 0·24 | .... | 1·10 |
| $Al^2O^3$ | 4 | 205·6 | 17·79 | .... | 17·65 | 15·24 | .... | 16·54 |
| $SiO^2$ | 18 | 558·0 | 48·29 | .... | 48·74 | 47·04 | .... | 46·65 |
| HO | 18 | 162·0 | 14·03 | .... | 14·66 | 14·92 | .... | 15·25 |
| | 1 | 1155·4 | 100·00 | .... | 100·27 | 100·11 | .... | 99·76 |

η. *Brewsterite.*—$3(BaO; SrO; CaO), 4Al^2O^3, 18SiO^2, 15Aq. = 3([BaO; SrO; CaO], 2SiO^2) + 4(Al^2O^3, 3SiO^2) + 15Aq$. Crystalline system, the oblique prismatic. Primary form, *Fig.* 81, with the faces $a$, $u$, $u^1$, $t$, and other lateral faces; the angle between $a$ and $a$, and the angle between $u^1$ and $u = 93° 40'$; $a^1 : t = 93° 30'$; $u^1 : u = 131°$; $u : t = 114° 30$; cleavage parallel to $t$. (Brooke.) Specific gravity from 2·12 to 2·2. (Brewster.) Transparent and colourless. According to Connell, it is but imperfectly decomposed by hydrochloric acid.

| | At. | *Brewsterite.* | | | Connell. Strontian. |
|---|---|---|---|---|---|
| NaO | .... | | | .... | trace |
| BaO | 2 | .... | 153·2 | 7·18 | .... 6·75 |
| SrO | 3 | .... | 156·0 | 7·31 | .... 8·32 |
| CaO | 1 | .... | 28·0 | 1·31 | .... 1·35 |
| $Fe^2O^3$ | .... | | | .... | 0·29 |
| $Al^2O^3$ | 8 | .... | 411·2 | 19·26 | .... 17·49 |
| $SiO^2$ | 36 | .... | 1116·0 | 52·29 | .... 53·67 |
| HO | 30 | .... | 270·0 | 12·65 | .... 12·58 |
| | 1 | .... | 2134·4 | 100·00 | .... 100·45 |

θ. *Heulandite, Lamellar Zeolite.* — $3CaO, 4Al^2O^3, 21SiO^2, 20Aq. = 3(CaO, 3SiO^2) + 4(Al^2O^3, 3SiO^2) + 20Aq$. Primary form, a right rhombic prism: $u^1 : u = 129° 50'$. Resembles stilbite. It is readily decomposed by hydrochloric acid, the silica being separated in the form of a viscid powder.

| | At. | *Heulandite.* | | Rammelsberg. | | Walmstedt. | | Thomson. |
|---|---|---|---|---|---|---|---|---|
| CaO | 3 | .... 84·0 | 7·49 | .... | 7·2 | .... 7·13 | .... | 7·65 |
| $Fe^2O^3$ | .... | | | .... | | .... 0·20 | .... | |
| $Al^2O^3$ | 4 | .... 205·6 | 18·35 | .... | 17·6 | .... 17·08 | .... | 17·92 |
| $SiO^2$ | 21 | .... 651·0 | 58·09 | .... | 58·2 | .... 60·07 | .... | 59·14 |
| HO | 20 | .... 180·0 | 16·07 | .... | 16·0 | .... 15·10 | .... | 15·40 |
| | 1 | .... 1120·6 | 100·00 | .... | 99·0 | .... 99·58 | .... | 100·11 |

¶ *k. Two atoms of stronger base to three atoms of alumina.*

*Diphanite.*—$2(2MO, SiO^2) + 3(2Al^2O^3, SiO^2) + 4HO$; or, $2(4MO, 3SiO^2) + 3(4Al^2O^3, 3SiO^2) + 8HO$. A mineral occurring in the emerald mines of the Uralian mountains, together with emerald, cymophane, and phenakite, on a brown micaceous slate. Forms regular six-sided prisms, with a distinct plane of cleavage at right angles to the principal axis. The prisms appear blue and transparent on one side, and have a vitreous lustre; on the cleavage-faces, however, the mineral appears white and opaque when in tolerably thick laminæ, and has a mother-of-pearl lustre. Its name is derived from this peculiarity (δὶς and φαίνω). Hardness from 5 to 5·5; very brittle; specific gravity 3·04 to 3·07.

When heated, it acquires a darker colour, emits a burnt odour, and deposits moisture on the sides of the glass. Before the blowpipe it becomes opaque, swells up, exfoliates, and fuses in the inner flame to a smooth enamel. With borax and microcosmic salt, it readily yields a clear glass which acquires a yellowish tinge on cooling; with the latter salt also a skeleton of silica is left undissolved. With a small quantity of carbonate of soda, it yields a blistered glass which is dark on the surface; with a larger quantity, an infusible enamel slightly coloured by manganese.

| | At. | | *Diphanite.* | | | Jewreinoff. |
|---|---|---|---|---|---|---|
| CaO ..... | 4 | .... | 89·6 | 13·11 | .... | 13·11 |
| FeO ..... | | | 21·6 | 3·04 | .... | 3·02 |
| MnO ..... | | | 7·2 | 1·13 | .... | 1·05 |
| $Al^2O^3$ ..... | 6 | .... | 308·4 | 44·33 | .... | 43·33 |
| $SiO^3$ ..... | 5 | .... | 232·5 | 33·21 | .... | 34·02 |
| HO ..... | 4 | .... | 36·0 | 5·18 | .... | 5·34 |
| | 1 | .... | 695·3 | 100·00 | .... | 99·87 ¶ |

*l. One atom of stronger base with from* 2 *to* 2½ *atoms of alumina.*

To this division appear to belong *Poonalite, Rosellane, Polyargite, Gigantolite, Rosite, Oncosine,* and *Pyrophyllite.*

¶ *Castor* and *Pollux.*—Two new minerals closely allied to each other, discovered by Breithaupt, and further examined by Plattner (*Pogg.* 69, 436 and 443). Found in the granite of the island of Elba.—*Castor* $LO, SiO^3 + 2(Al^2O^3, 2SiO^3)$ has a high glassy lustre, is transparent and colourless, and biaxial. Primary form, a modified rhombic prism not before observed. Hardness between 8¼ and 8½, or rather greater than that of adularia. Specific gravity 2·39. In the direction of its two planes of cleavage, in hardness, and in density, Castor somewhat resembles petalite. Heated in a test-tube, it neither changes in appearance nor gives off water. When heated in thin laminæ before the blowpipe, it fuses with difficulty, yielding a transparent, colourless bead; imparts an intense carmine colour to the outer flame. When powdered, it dissolves in borax with tolerable facility, forming a glass which is yellowish while hot but colourless when cold. In microcosmic salt it dissolves in a similar manner, with the exception of a portion of silica; the glass becomes opalescent on cooling. With carbonate of soda, it effervesces and yields a clear colourless bead. The finely divided mineral moistened with solution of cobalt and exposed to the outer flame on charcoal, is coloured blue where complete fusion takes place. It is scarcely attacked by hydrochloric acid.—*Pollux.* $3(KO, SiO^3) + 3(NaO, SiO^3) + 3(Al^2O^3, SiO^3) + 2HO$. Lustre and other physical characters like those of Castor. Its form is greatly broken and resembles that of Castor, excepting that the edges are less acute, and frequently even rounded like those of hyalite. Fracture conchoidal. Cleavage scarcely perceptible, if any. Heated in a glass tube, it evolves water, and loses its transparency, so that it appears opalescent when cold. Before the blowpipe it becomes white, and—when in thin laminæ—rounded at the edges, the fused portions resembling a blistered enamel; colours the outer flame reddish-yellow. Dissolves readily in borax and microcosmic salt, forming a transparent glass similar to that formed by Castor. With carbonate of soda, it effervesces and yields a clear bead, which, if fused with a larger quantity of the carbonate, sinks almost wholly into the

charcoal, leaving only a small opaque bead, which, if similarly treated, is completely absorbed. Hydrochloric acid, with the aid of heat, decomposes it perfectly, the silica being separated in the state of powder.

| | At. | | *Castor.* | | Plattner. | At. | | *Pollux.* | | Plattner. |
|---|---|---|---|---|---|---|---|---|---|---|
| KO | .... | .... | | .... | | .... 3 | .... | 141·6 | 17·20 | .... 16·51 |
| NaO | .... | .... | | .... | | .... 3 | .... | 93·6 | 11·39 | .... 10·47 |
| LO | 1 | .... | 14·4 | 2·71 | .... 2·76 | .... | .... | | | .... |
| $Al^2O^3$ | 2 | .... | 102·8 | 19·29 | .... 18·86 | .... 3 | .... | 154·2 | 18·74 | .... 16·39 |
| $Fe^2O^3$ | .... | .... | | .... | 0·61 | .... | .... | | | .... 0·86 |
| $SiO^2$ | 5 | .... | 232·5 | 78·00 | .... 78·01 | .... 9 | .... | 418·5 | 50·49 | .... 46·20 |
| HO | .... | .... | | .... | .... 2 | .... | | 18·0 | 2·18 | .... 2·32 |
| | 1 | .... | 349·7 | 100·00 | .... 100·24 | .... 1 | .... | 825·9 | 100·00 | .... 92·75 |

The formulæ for these two minerals, supposing silica $= SiO^2$, are respectively: $2LO, 3SiO^2 + 4(Al^2O^3, 3SiO^2)$ and $3(KO, \frac{3}{2}SiO^2) + 3(NaO, \frac{3}{2}SiO^2) + 3(Al^2O^3, \frac{3}{2}SiO^2) + 2HO$. The loss in the analysis of Pollux, Plattner could not account for, as he found neither chlorine nor fluorine in mineral. (A repetition of the whole process was impossible, on account of the small quantity of the mineral obtained.) Pollux appears to contain a larger quantity of alkali than any other known mineral. ¶

*m. One atom of stronger base with* 3 *atoms of alumina.*

*Biaxial* or *Potash-mica.*—Crystalline system the oblique prismatic; oblique rhombic and short six-sided prisms; $u^1 : u = 119°....120°$; cleaves very readily parallel to *i*, in thin, elastic laminæ. Sp. gr. from 2·8 to 3·0; hardness between gypsum and calcareous spar. Transparent; biaxial in polarized light; colourless or light-coloured with metallic, pearly lustre. When richer in fluorine it loses lustre by ignition, a small quantity of water and generally also of hydrofluoric acid being evolved. Fuses with variable degrees of facility to a turbid glass or a white enamel. (Berzelius.) Not decomposed either by hydrochloric or by sulphuric acid.

The formula appears in general to be $KO, 3Al^2O^3, 6SiO^2 = (KO, 3SiO^2) + 3(Al^2O^3, SiO^2)$. A portion of the potash is, however, replaced by lime, protoxide of manganese, and protoxide of iron, and a portion of the alumina by the sesquioxide of iron, manganese, or chromium. The mica also contains small variable quantities of metallic fluorides and of water; but it has not been ascertained whether these substances are essential constituents of the mineral or merely accidental admixtures. The following calculations of a few analyses are given in confirmation of the above formula.

| | At. | | *Biaxial Mica.* | | H. Rose. Utön. | | Kimito. |
|---|---|---|---|---|---|---|---|
| KO | 5 | .... | 236·0 | 10·09 | .... 9·60 | .... | 9·22 |
| FeO | 1 | .... | 35·2 | 1·50 | .... *0·90 | .... | |
| $Fe^2O^3$ | 1 | .... | 78·4 | 3·35 | .... 3·20 | .... | 4·54 |
| $Al^2O^3$ | 17 | .... | 873·8 | 37·36 | .... 37·20 | .... | 36·80 |
| $SiO^2$ | 36 | .... | 1116·0 | 47·70 | .... 47·50 | .... | 46·36 |
| F—O | | .... | | | .... 0·56 | .... | 0·77 |
| HO | | .... | | | .... 2·63 | .... | 1·84 |
| | 1 | .... | 2339·4 | 100·00 | .... 101·59 | .... | 99·53 |

| | At. | | | | | H. Rose. Broddbo. | | Svanberg. |
|---|---|---|---|---|---|---|---|---|
| KO | 3 | .... | 141·6 | 8·90 | .... | 8·39 | .... | 8·31 |
| FeO | 1 | .... | 35·2 | 2·21 | .... | *1·40 | .... | *1·67 |
| $Fe^2O^3$ | 2 | .... | 156·8 | 9·85 | .... | 8·65 | .... | 5·37 |
| $Al^2O^3$ | 10 | .... | 514·0 | 32·29 | .... | 31·60 | .... | 32·35 |
| $SiO^2$ | 24 | .... | 744·0 | 46·75 | .... | 46·10 | .... | 47·97 |
| F—O | | .... | | | .... | 1·12 | .... | 0·42 |
| HO | | .... | | | .... | 1·00 | .... | 3·32 |
| | 1 | .... | 1591·6 | 100·00 | .... | 98·26 | .... | 99·41 |

| | At. | | | | | H. Rose. Fahlun. | | Ochotzk. |
|---|---|---|---|---|---|---|---|---|
| KO | 2 | .... | 94·4 | 8·02 | .... | 8·22 | .... | 8·35 |
| FeO | 1 | .... | 35·2 | 2·99 | .... | *2·11 | .... | *2·58 |
| $Fe^2O^3$ | 1 | .... | 78·4 | 6·66 | .... | 6·04 | .... | 4·47 |
| $Al^2O^3$ | 8 | .... | 411·2 | 34·93 | .... | 34·52 | .... | 33·80 |
| $SiO^2$ | 18 | .... | 558·0 | 47·40 | .... | 46·22 | .... | 47·19 |
| F—O | | .... | | | .... | 1·09 | .... | 0·29 |
| HO | | .... | | | .... | 0·98 | .... | 4·07 |
| $TiO^2$ | | .... | | | .... | trace | CuO | 0·13 |
| | 1 | .... | 1177·2 | 100·00 | .... | 99·18 | .... | 100·88 |

| | At. | | | | | Schaffhäutl. *Fuchsite.* | | *Chrome-mica.* |
|---|---|---|---|---|---|---|---|---|
| KO | 20 | .... | 944·0 | 10·02 | .... | 10·75 | .... | 7·27 |
| NaO | 1 | .... | 31·2 | 0·33 | .... | 0·37 | .... | 1·17 |
| MgO | 3 | .... | 60·0 | 0·64 | .... | 0·71 | .... | 11·58 |
| $Cr^2O^3$ | 5 | .... | 401·0 | 4·25 | .... | 3·95 | .... | 5·91 |
| $Fe^2O^3$ | 3 | .... | 235·2 | 2·49 | .... | 1·80 | .... | 5·72 |
| $Al^2O^3$ | 64 | .... | 3289·6 | 34·90 | .... | 34·45 | .... | 15·15 |
| $SiO^2$ | 144 | .... | 4464·0 | 47·37 | .... | 47·95 | .... | 47·68 |
| CaF | | .... | | | .... | 0·78 | .... | traces |
| $Mn^2O^3$ | | .... | | | .... | | .... | 1·16 |
| HO | | .... | | | .... | | .... | 2·87 |
| | 1 | .... | 9425·0 | 100·00 | .... | 100·76 | .... | 98·51 |

The numbers marked with an asterisk signify $Mn^2O^3$ in Rose's analyses, and MnO in those of Svanberg. — In *Fuchsite* or *Chrome-mica* a portion of the alumina is replaced by sesquioxide of chromium. ¶ Schaffhäutl gives for *Fuchsite* the formula $38(3KO, SiO^3)+2(3NaO, SiO^3)+360(Al^2O^3, SiO^3)+24(Cr^2O^3, 3SiO^3)+18(MgO, SiO^3)+12(Fe^2O^3, 3SiO^3)+9CaF^2$; and for *chrome-mica* $4(KO, SiO^2)+NaO, SiO^2+4(2Al^2O^3, SiO^3)+2Cr^2O^3, 3SiO^3+7(2MgO, SiO^2)+2Fe^2O^3, 3SiO^3+\frac{2}{3}M^2O^3, \frac{1}{3}SiO^3+8HO$.

Schaffhäutl (*Ann. Pharm.* 46, 325) describes Fuchsite as being found in compact, scaly, and likewise regular slaty masses, frequently accompanied by pure quartz. Specific gravity = 2·86; hardness between gypsum and rock salt; colour emerald green, passing into dull yellow. With soda before the blowpipe it swells up and fuses to a yellowish-brown globular slag, which, after continued exposure to the flame, acquires a dull green colour, and is slightly affected by the magnet. In borax it is dissolved slowly, forming a clear bead, which is yellow while hot (from the presence of ferric oxide), but when cold assumes a fine yellowish-green colour due to the chromium. Microcosmic salt dissolves the mineral readily, forming a bluish-green glass when cold. It resists the action of all acids excepting the hydrofluoric. *Chrome-mica* closely resembles uniaxial

magnesia-mica, but has a duller green colour; it is easily bent between the fingers like chlorite, and is friable in small pieces; specific gravity $=2{\cdot}75$ at 4°. Before the blowpipe it fuses only when in very thin scales; larger pieces are merely rounded at the edges. With borax and microcosmic salt it yields a beautiful emerald-green bead; it is perfectly decomposed by acids, especially by hydrochloric acid.

Schaffhäutl has likewise examined the following minerals, which are allied to biaxial mica:

*Paragonite* (*Talc-slate, Hardened Talc, Mica-slate*).—$24(Al^2O^3, SiO^3) + 9(NaO, SiO^3) + (Fe^2O^3, 3SiO^3)$. Specific gravity $= 2{\cdot}78$ at 4°. Somewhat harder than rock-salt; easily scraped with a knife; of a yellowish and greyish-white colour; glittering; translucent at the corners; slightly unctuous to the touch. Does not change in the blowpipe flame. Borax dissolves it, forming a clear glass. With microcosmic salt it leaves an opaque skeleton of silica. Solution of cobalt colours it blue. It is not acted on by acids.

*Margarodite.* (*Margarite, Hardened Talc.*)—$12(3Al^2O^3, 2SiO^3) + 3(MgO, 2SiO^3) + Fe^2O^3, 3SiO^3 + 6(NaO, SiO^3) + 9(KO, SiO^3)$. Dull green, passing into bright green; rarely occurring in fine-grained laminæ, in which case it much resembles mica. Specific gravity $= 2{\cdot}87$; hardness between rock-salt and calc-spar; easily pulverized; slightly translucent at the edges. It has sometimes an opalescent, sometimes a mother-of-pearl lustre. In fine laminæ it fuses before the blowpipe, emitting a vivid light and yielding a white enamel. With borax it yields a colourless glass. Microcosmic salt dissolves it in a similar manner, with separation of silica. Solution of cobalt partially colours it faint blue. Acids have no perceptible action on it. Margarodite forms the matrix of the black tourmaline from the Zillerthal, and was probably regarded as ordinary talc.

*Nephrite.*—$[21(2MgO, SiO^3) + 3(CaO, 2SiO^3), \frac{1}{2}(KO, SiO^2)] + [Al^2O^3, 6SiO^3 + Fe^2O^3, 6SiO^3 + \frac{1}{2}(Mn^2O^3, 2SiO^3)]$.—Dense, with dull splintered fracture; appears of a dirty yellowish-green colour by transmitted light. Takes a very good polish and scratches glass. Very difficult to break. Specific gravity 2·96 at 4°. (Schaffhäutl, *Ann. Pharm.* 46, 325.)

*Baulite.*—Described by Forchhammer as occurring, mixed with quartz, on the Baula Mountain in Iceland. According to the same authority it is the hydrate of an unknown felspar, in which the quantity of oxygen in the bases MO is to that of the alumina and silica as 1 : 3 : 18 or 1 : 3 : 20. Crystalline system the oblique prismatic; cleavage indistinct; fracture uneven, inclining to the conchoidal; hardness between 5·5 and 6. Specific gravity 2·656 at 6°. Transparent and colourless, sometimes translucent, and with a glassy lustre. Yields colourless glasses with borax and microcosmic salt; in the latter case, a skeleton of silica is separated. The mineral is insoluble in hydrochloric acid.

*Phillipsite.*—Found near Marburg. White passing into yellow, and of glassy lustre. Frequently occurs in intersecting macle-crystals composed of an oblique prism, and a regular octohedron. (Genth, *Ann. Pharm.* 66, 270.)

| | Schaffhäutl. | | Forchhammer, Genth. | | |
|---|---|---|---|---|---|
| | *Paragonite.* | *Margarodite.* | *Nephrite.* | *Baulite.* | *Phillipsite.* |
| KO | | 7·96 | 0·800 | 4·92 | 6·61 |
| NaO | 8·45 | 4·07 | | 2·26 | 0·63 |
| CaO | | | 12·151 | 0·95 | 6·97 |
| BaO | | | | | traces |
| MgO | | 1·95 | 22·387 | traces | |
| $Al^2O^3$ | 35·90 | 34·90 | 1·564 | 12·08 | 21·11 |
| $Mn^2O^3$ | | | 0·828 | traces | 0·24 |
| $Fe^2O^3$ | 2·36 | 1·50 | 2·811 | | |
| $SiO^2$ | 50·20 | 47·05 | 58·885 | 50·23 | 48·17 |
| HO | 2·45 | 1·45 | 0·268 | | 16·62 |
| | 99·36 | 98·88 | 99·694 | 70·44 | 100·35 ¶ |

*n. One atom of stronger base with 4 atoms of alumina.*

Many varieties of *Agalmatolite* appear to consist of $KO, 3SiO^2 + 4(Al^2O^3, 2SiO^2) + 3Aq.$; the potash being partially replaced by lime.

| | At. | *Agalmatolite.* | | Vauquelin. *Yellow.* | Klaproth. *Greenish-white.* | John. *Red.* |
|---|---|---|---|---|---|---|
| KO | 1 | 47·2 | 7·60 | 7 | 6·25 | 5·25 |
| CaO | | | | 2 | | 2·00 |
| $Fe^2O^3$ | | | | 1 | 0·75 | 1·25 |
| $Al^2O^3$ | 4 | 205·6 | 33·12 | 29 | 34·00 | 31·00 |
| $SiO^2$ | 11 | 341·0 | 54·93 | 56 | 54·50 | 55·50 |
| HO | 3 | 27·0 | 4·35 | 5 | 4·00 | 5·00 |
| | 1 | 620·8 | 100·00 | 100 | 99·50 | 100·00 |

D. Compounds of double Silicate of Alumina and another base with Carbonates, Borates, or Sulphates, or with metallic Sulphides, Chlorides, or Fluorides.

*a. Combinations with Carbonates.*

*Cancrinite.*—According to Breithaupt this mineral is identical with *Davyne.*—$5NaO, 5Al^2O^3, 11SiO^2, 2(CaO, CO^2)$ = one atom of Elaeolite + 2 atoms of carbonate of lime.—Dense; cleavage parallel to the faces of a regular six-sided prism. Specific gravity = 2·453. Before the blowpipe it gives a white, blistered glass. Dissolves in hydrochloric acid with violent effervescence and formation of a jelly. (G. Rose.)

¶ Whitney (*Pogg.* 70, 443) gives the following particulars relating to the cancrinite obtained from Litchfield, in the State of Maine, U. S. Hardness 5·5 to 6. Specific gravity = 2·448; lemon-yellow or sulphur-yellow sometimes also greenish; of a vitreous lustre at the fractured surfaces, and of an unctuous appearance in the other parts; transparent or translucent. When heated it gives off water, and instantly loses its colour; at a red heat it becomes white and opaque. Before the blowpipe it fuses with considerable effervescence, and yields a transparent, colourless, and blistered glass. With soda it yields an opaque bead coloured by manganese. Borax and microcosmic salt dissolve it; in the former case a transparent glass is produced; in the latter a glass which becomes milky when cold. With solution of cobalt it gives a splendid blue colour.

*Amphilogite* or *Didrimite.*—(Talc-slate)—$12(CaO, CO^2) + 5(2Al^2O^3, SiO^3) + 4(Fe^2O^3, 3SiO^3) + 6(KO, SiO^3) + NaO, SiO^3$, or (silica = $SiO^2$), $24(CaO, CO^2) + 5(4Al^2O^3, 3SiO^2) + 4(2Fe^2O^3, 9SiO^2) + 6(2KO, 3SiO^2) + 2NaO^3, SiO^2$. From the Zillerthal in the Tyrol. Crystalline; of delicate, scaly texture; slaty when in large masses. Specific gravity = 2·75 at 4°.

Scarcely harder than gypsum; easily scratched by the nail; very friable, and unctuous to the touch when pulverized. Colour greenish white; lustre somewhat like that of mother-of-pearl; translucent at the edges. A small fragment fuses before the blowpipe with vivid light and yields a white, enamel-like bead. Borax dissolves it with difficulty, forming a clear glass, which is yellowish while hot, from the presence of iron. With microcosmic salt it effervesces and then dissolves, leaving, however, a skeleton of silica. Solution of cobalt imparts a fine blue colour to it. Effervesces strongly with hydrochloric acid. (Schaffhäutl, *Ann. Pharm.* 46, 325.) ¶

| | At. | *Cancrinite.* | | Whitney. From Litchfield. *Yellow.* | *Green.* | G. Rose. | Schaffhäutl. *Amphilogite.* |
|---|---|---|---|---|---|---|---|
| KO | .... | | .... | 0·67 | 0·50 | 0·82 | 11·16 |
| NaO | 5 | 156 | 18·27 | 20·98 | 20·46 | 17·66 | 1·23 |
| $Al^2O^3$ | 5 | 257 | 30·09 | 27·70 | 27·56 | 28·24 | 18·15 |
| $Fe^2O^3$ | .... | | .... | trace | 0·27 | .... | 5·25 |
| $Mn^2O^3$ | .... | | .... | 0·86 | | | |
| $SiO^2$ | 11 | 341 | 39·93 | 37·42 | 37·20 | 40·26 | 40·69 |
| CaO | 2 | 56 | 6·56 | 3·91 | 5·26 | 6·34 | 22·74 |
| $CO^2$ | 2 | 44 | 5·15 | 8·77 | 9·20 | 6·38 | |
| HO | .... | | | | | | 0·61 |
| Cl | .... | | .... | trace | trace | | |
| | 1 | 854 | 100·00 | 100·31 | 100·45 | 99·70 | 99·83 |

### *b. Combinations with Borates.*

*a. Axinite.*—6(CaO; MgO; MnO; FeO), 2($Fe^2O^3$; $Al^2O^3$), 8$SiO^2$, 1$BO^3$ = 4[(CaO; MgO; MnO; FeO), $SiO^2$] + 2[($Fe^2O^3$; $Al^2O^3$), 2$SiO^2$] + (2CaO, $BO^3$).—Crystalline system the doubly oblique prismatic. *Fig.* 124, 125, and other forms; $y : v = 135°$; $y : u = 136° 14'$; $v : u = 116° 54'$. (Hauy.) Specific gravity = 3·294; harder than felspar. When fused in a crucible it does not lose weight, but its specific gravity is reduced from 3·294 to 2·815. (Rammelsberg.)—Swells up before the blowpipe, and fuses to a dark-green glass, which becomes black in the outer flame, in consequence of the manganese passing to a higher degree of oxidation. Dissolves readily in borax, forming a glass which is coloured by iron, but takes an amethyst colour in the outer flame; with microcosmic salt, the same colour is produced and an insoluble skeleton of silica separated. With carbonate of soda it first becomes green and then fuses to a black glass, having almost a metallic lustre. (Berzelius.) Mixed with fluorspar and bisulphate of potash, it colours the blowpipe flame green. (Turner.) In the native state it almost wholly resists the action of acids; but after fusion and pulverization, it is perfectly decomposed, with formation of a jelly. (Rammelsberg.)

| | At. | *Axinite.* | | | Rammelsberg. Dauphiné. | Harz. | Ural. |
|---|---|---|---|---|---|---|---|
| KO | .... | | | .... | 0·64 | | |
| CaO | 16 | 448·0 | 19·72 | .... | 20·67 | 18·90 | 19·97 |
| MgO | 2 | 40·0 | 1·76 | .... | 1·70 | 1·77 | 2·21 |
| MnO | 2 | 73·2 | 3·22 | $Mn^2O^3$ | 3·05 | 1·37 | 1·16 |
| FeO | 4 | 140·8 | 6·19 | | | | |
| $Fe^2O^3$ | 1 | 78·4 | 3·47 | .... | 9·45 | 11·94 | 10·21 |
| $Al^2O^3$ | 7 | 359·8 | 15·84 | .... | 15·63 | 15·66 | 16·92 |
| $SiO^2$ | 32 | 992·0 | 43·67 | .... | 43·68 | 43·74 | 43·72 |
| $BO^3$ | 4 | 139·2 | 6·13 | .... | 5·61 | 6·62 | 5·81 |
| | 1 | 2271·4 | 100·00 | .... | 100·43 | 100·00 | 100·00 |

Rammelsberg estimates the whole of the manganese and iron contained in axinite as sesquioxides; but the behaviour of the mineral before the blowpipe is opposed to this assumption.

*β. Tourmaline, Schörl.* — Primary form, an obtuse rhombohedron, *Fig.* 141, $r^3 : r^5 = 133° 28'$; three, six, and nine-sided prisms with the faces of different rhombohedrons, the *P*-face and others also having unsymmetrical terminations; cleavage parallel to *r*; sp. gr. from 3·0 to 3·3; softer than quartz. Exhibits every degree of transparency, from perfect clearness to complete opacity, and is also variously coloured. Swells up before the blowpipe, and fuses to a slag when the flame is strongly urged; the variety called *Apyrite*, however, does not fuse. When finely divided tourmaline is boiled with oil of vitriol and the residue digested with alcohol, the alcohol dissolves out boracic acid and burns with a green flame; hydrochloric acid is far from effecting complete decomposition.

a. *Soda-tourmaline, Ordinary Schörl.*—Green or black. The three analyses made by C. Gmelin cannot be reduced to a common formula. The simplest that can be reduced to calculation are:

| | NaO | $Al^2O^3$ | $SiO^2$ | $BO^3$ |
|---|---|---|---|---|
| Green tourmaline from Chesterfield | 3 | 8 | 12 | 1 |
| Black from Bovey | 6 | 8 | 12 | 1 |
| Black from Eibenstock | 8 | 8 | 12 | 1 |

NaO is partially replaced by KO, CaO, MgO, MnO, and FeO; and $Al^2O^3$ by $Fe^2O^3$. The analysis of the Chesterfield tourmaline is given as an example.

| | At. | *Soda-tourmaline.* | | C. Gmelin. Chesterfield. | | Bovey. | Eibenstock. |
|---|---|---|---|---|---|---|---|
| NaO | 6 | 187·2 | 4·99 | 4·95 | | 2·09 | 3·17 |
| CaO | | | | | | 0·55 | 0·86 |
| MnO | 3 | 106·8 | 2·85 | 2·88 | & MgO | 1·13 | |
| FeO | 3 | 105·6 | 2·81 | 7·43 | | 17·86 | 23·86 |
| $Fe^2O^3$ | 3 | 235·2 | 6·27 | | | | |
| $Al^2O^3$ | 29 | 1490·6 | 39·72 | 39·61 | | 35·50 | 38·23 |
| $SiO^2$ | 48 | 1488·0 | 39·65 | 38·80 | | 35·20 | 33·05 |
| $BO^3$ | 4 | 139·2 | 3·71 | 3·88 | | 4·11 | 1·89 |
| Loss by ignition | | | | 0·78 | | | 0·45 |
| | 1 | 3752·6 | 100·00 | 98·33 | | 96·44 | 101·51 |

The Bovey tourmaline consists of: 2NaO, 1CaO, 1MgO, 14FeO, (total 18),—$2Fe^2O^3$, $22Al^2O^3$ (total 24),—$36SiO^2$—$4Bo^3$; that from Eibenstock, of: 3NaO, 21FeO (total 24),—$24Al^2O^3$,—$36SiO^2$—$3BO^3$.

b. *Tourmaline richer in magnesia*, has sometimes the same, and sometimes very similar formulæ:

| | MgO | $Al^2O^3$ | $SiO^2$ | $BO^3$ |
|---|---|---|---|---|
| A brown variety from St. Gothard, and a black variety from Greenland | 4 | 8 | 12 | 1 |
| A black variety from Käringsbricka and Rabenstein | 6 | 8 | 12 | 1 |

The MgO is partially replaced by KO, NaO, CaO, MnO, and FeO, and the $Al^2O^3$ by $Fe^2O^3$.

The following calculations are added in confirmation of the formulæ.

| | At. | *Magnesia-tourmaline.* | | C. Gmelin. Greenland. | | St. Gothard. |
|---|---|---|---|---|---|---|
| KO | | | | 0·22 | .... | 1·20 |
| NaO | 4 | 124·8 | 3·45 | 3·13 | CaO | 0·98 |
| MgO | 12 | 240·0 | 6·63 | 5·86 | .... | 5·99 |
| $Mn^2O^3$ | | | | trace | .... | 1·11 |
| FeO | | | | | | |
| $Fe^2O^3$ | 3 | 235·2 | 6·50 | 5·81 | .... | 7·77 |
| $Al^2O^3$ | 29 | 1390·6 | 38·44 | 37·19 | .... | 31·61 |
| $SiO^2$ | 48 | 1488·0 | 41·13 | 38·79 | .... | 37·81 |
| $BO^3$ | 4 | 139·2 | 3·85 | 3·63 | .... | 4·18 |
| Loss by ignition | | | | 1·86 | .... | 0·24 |
| | 1 | 3617·8 | 100·00 | 96·49 | .... | 90·89 |

| | At. | *Magnesia-tourmaline.* | | C. Gmelin. Rabenstein. | | Käringsbricka. |
|---|---|---|---|---|---|---|
| KO | | | | 0·48 | .... | 2·53 |
| NaO | 3 | 93·6 | 2·30 | 1·75 | | |
| MgO | 9 | 180·0 | 4·42 | 4·68 | .... | 10·98 |
| MnO | 2 | 71·2 | 1·75 | 1·89 | CaO | 0·25 |
| FeO | 10 | 352·0 | 8·63 | 17·44 | .... | 9·38 |
| $Fe^2O^3$ | 4 | 313·6 | 7·69 | | | |
| $Al^2O^3$ | 28 | 1439·2 | 35·30 | 34·75 | .... | 33·46 |
| $SiO^2$ | 48 | 1488·0 | 36·50 | 35·48 | .... | 37·65 |
| $BO^3$ | 4 | 139·2 | 3·41 | 4·02 | .... | 3·83 |
| Loss by ignition | | | | | .... | 0·03 |
| | 1 | 4076·8 | 100·00 | 100·49 | .... | 98·11 |

The tourmaline of Käringsbricka consists of about: $2NaO, 16MgO$ (total 18),—$4Fe^2O^3, 20Al^2O^3$ (total 24),—$36SiO^2$,—$3BO^3$.

c. *Lithia-tourmaline, Apyrite, Rubellite, Siberite.*—The analyses of this mineral likewise yield very indefinite formulæ.

| | C. Gmelin. Perm. | | Brazil. | | Rozna. |
|---|---|---|---|---|---|
| KO | 1·29 | .... | 3·59 | .... | 2·41 |
| LiO | 2·52 | | | .... | 2·04 |
| CaO | | .... | | .... | 1·20 |
| $Mn^2O^3$ | 5·02 | .... | 2·14 | .... | 6·32 |
| $Fe^2O^3$ | | .... | 5·96 | | |
| $Al^2O^3$ | 44·00 | .... | 40·00 | .... | 36·43 |
| $SiO^2$ | 39·37 | .... | 39·16 | .... | 42·13 |
| $BO^3$ | 4·18 | .... | 4·59 | .... | 5·74 |
| Loss by ignition | 1·58 | .... | 1·58 | .... | 1·31 |
| | 97·96 | .... | 97·02 | .... | 97·58 |

The tourmaline of Perm is composed of about: $1KO, 6LiO, 5MnO$ (total 12),—$32Al^2O^3$,—$48SiO^2$,—$4BO^3 = 3 : 8 : 12 : 1$.

That from the Brazils: $1KO, 1LiO, 1MnO, 1FeO$ (total 4),—$1Fe^2O^3$, $15Al^2O^3$ (total 16),—$24SiO^2$,—$2BO^3 = 2 : 8 : 12 : 1$.

That of Rozna: $1KO, 3LiO, 1CaO, 3MnO$ (total 8),—$12Al^2O^3$,—$24SiO^2$,—$2BO^3 = 4 : 6 : 12 : 1$. This formula is distinguished from all the others by containing only 6 atoms of $Al^2O^3$, instead of 8 atoms in

combination with 12 atoms of $SiO^2$. Generally speaking, all the formulæ given for tourmaline must be regarded as merely approximative.

### *c. Combinations with Sulphates.*

The sulphate which occurs in this class of minerals is probably sulphate of lime, or perhaps also a kind of alum. They likewise contain a small quantity of some metallic sulphide, which generally gives them a blue colour. But whether this substance is sulphide of iron or sulphide of aluminum, or double sulphide of aluminum and iron, or double sulphide of iron and sodium, &c. has not yet been determined; we only know that on the addition of an acid, sulphuretted hydrogen is evolved and the mineral becomes colourless. All the minerals enumerated under this head probably belong to one species, whose primary form is a rhombic dodecahedron.

*α. Ittnerite.*—Cleavage indistinct, parallel to the faces of a rhombic dodecahedron. Sp. gr. 2·3; harder than apatite. Grey. (Breithaupt.) When gently heated it becomes covered with blue spots like stars. Swells up strongly before the blowpipe, and readily fuses, with evolution of sulphurous acid, to a blistered enamel. With borax and microcosmic salt, it yields a transparent glass, in the latter case containing a skeleton of silica. Boiling water dissolves out sulphate of lime. The mineral dissolves in hydrochloric acid, with evolution of sulphuretted hydrogen gas and formation of a siliceous jelly. (C. Gmelin.)

| | At. | | *Ittnerite.* | | | C. Gmelin. |
|---|---|---|---|---|---|---|
| KO | 1 | .... | 47·2 | 1·70 | .... | 1·57 |
| NaO | 10 | .... | 312·0 | 11·28 | .... | 11·29 |
| CaO | 5 | .... | 140·0 | 5·06 | .... | 5·26 |
| $Fe^2O^3$ | | .... | | | .... | 0·62 |
| $Al^2O^3$ | 16 | .... | 822·4 | 29·72 | .... | 28·40 |
| $SiO^2$ | 32 | .... | 992·0 | 35·85 | .... | 34·02 |
| $CaO, SO^3$ | | .... | 136·0 | 4·92 | .... | 4·89 |
| NaCl | | .... | 29·3 | 1·06 | .... | 1·62 |
| HO | 32 | .... | 288·0 | 10·41 | .... | 10·76 |
| S | | .... | | | | |
| | 1 | .... | 2766·9 | 100·00 | .... | 98·43 |

Omitting the chloride of sodium: $8(KO; NaO; CaO), 8Al^2O^3, 16SiO^2 + 16Aq + CaO, SO^3 + 8[(KO; NaO; CaO), SiO^2 + Al^2O^3, SiO^2] + 16Aq + CaO, SO^2 + xFeS$ (?).

*β. Noseane, Nosine, Spinellane.*—Occurs in rhombic dodecahedrons; cleavage indistinct, parallel to the faces of that solid. Sp. gr. = 2·28; harder than apatite. Grey or brown. Becomes colourless when heated, and fuses to a blistered glass. Decomposed by hydrochloric acid, with evolution of sulphuretted hydrogen and formation of gelatinous silica.

| | At. | | *Noseane.* | | | Varrentrapp. | | Bergemann. | | |
|---|---|---|---|---|---|---|---|---|---|---|
| NaO | 2 | .... | 62·4 | 18·95 | .... | 17·84 | .... | 16·56 | .... | 12·24 |
| CaO | | .... | | | .... | 1·12 | .... | 1·14 | .... | 8·14 |
| MnO | | .... | | | .... | | .... | 1·00 | .... | 0·50 |
| FeO | | .... | | | .... | 0·05 | .... | 1·50 | .... | 1·15 |
| $Al^2O^3$ | 2 | .... | 102·8 | 31·23 | .... | 32·57 | .... | 29·25 | .... | 27·50 |
| $SiO^2$ | 4 | .... | 124·0 | 37·67 | .... | 35·99 | .... | 38·50 | .... | 37·00 |
| $SO^3$ | 1 | .... | 40·0 | 12·15 | .... | 9·17 | .... | 8·16 | .... | 11·56 |
| HO | | .... | | | .... | 1·85 | | | | |
| S | | .... | | | .... | | .... | 2·82 | .... | 1·41 |
| Cl | | .... | | | .... | 0·65 | .... | | | |
| | 1 | .... | 329·2 | 100·00 | .... | 99·24 | .... | 98·93 | .... | 99·50 |

1($NaO$; $CaO$), $2Al^2O^3$, $4SiO^2$, 1($NaO$; $CaO$), $SO^3$ (?). The above analyses cannot be reduced to exact calculation.

3. *Soda-hauyne.*—The same crystalline form. Sp. gr. = 2·47. Light blue. Before the blowpipe and with hydrochloric acid, it behaves like noseane.

*Potash-hauyne.*—Of similar character.

The analyses hitherto made of hauyne admit only of approximate calculation.

| | At. | | *Soda-hauyne.** | | | Varrentrapp. Niedermennig. |
|---|---|---|---|---|---|---|
| $NaO$ | 2 | .... | 62·4 | 9·18 | .... | 9·12 |
| $CaO$ | 3 | .... | 84·0 | 12·35 | .... | 12·55 |
| $Al^2O^3$ | 4 | .... | 205·6 | 30·23 | .... | 27·42 |
| $SiO^2$ | 8 | .... | 248·0 | 36·47 | .... | 35·01 |
| $SO^3$ | 2 | .... | 80·0 | 11·77 | .... | 12·60 |
| S | | .... | | | .... | 0·24 |
| Cl | | .... | | | .... | 0·58 |
| F | | .... | | | .... | 1·72 |
| HO | | .... | | | .... | 0·62 |
| | 1 | .... | 680·0 | 100·00 | .... | 99·86 |

*Lapis-lazuli* contains the same substances as soda-hauyne, but in different proportions.

From the lapis-lazuli, *Natural Ultramarine* is prepared by slightly igniting the mineral, slaking the mass in water, reducing it to fine powder, and mixing the powder with a melted resinous mass, called *pastello* (composed of linseed oil, wax, and resin), and kneading the whole well with cold water. Ultramarine is then deposited, having a deep blue colour at first, but afterwards a lighter colour. The iron pyrites and other impurities in the lapis-lazuli are retained by the resin. The otherwise very durable colour is destroyed by acids, with evolution of sulphuretted hydrogen gas. Ultramarine remains unaltered when boiled with baryta-water. Hydrogen gas passed over ignited ultramarine, colours it light red, from formation of liver of sulphur, hydrosulphuric acid gas and water being evolved at the same time.

*Artificial Ultramarine.*—1. A solution of caustic soda is saturated with precipitated silica. Alum freed by recrystallization from the greater part of the iron which it contains, is precipitated by carbonate of soda, and the hydrate, after being washed, is dried till the water which it retains amounts to 90 per cent. It is then added to the silicate of soda in such proportions, that 26 parts of anhydrous alumina shall be present for every 31 parts of anhydrous silica (with 14 to 33 parts of alumina to the 31 parts of silica, a beautiful blue is still obtained). The mixture is evaporated to dryness, with constant stirring, and the mass thus obtained is reduced to fine powder and mixed with flowers of sulphur: this is mixture $\alpha$. On the other hand, dry carbonate of soda and flowers of sulphur are mixed in equal quantities: this gives mixture

* ¶ Whitney (*Pogg.* 70, 443) gives the following comparative view of the formula for sodalite (p. 461), noseane, hauyne from the Albany mountains, and hauyne from Niedermennig (Silica = $SiO^3$).

| | |
|---|---|
| Sodalite | $3NaO, SiO^3 + (3Al^2O^3, SiO^3) + NaCl$. |
| Noseane | $3NaO, SiO^3 + 3(Al^2O^3, SiO^3) + NaO, SO^3$. |
| Hauyne from the Albany mountains | $3NaO, SiO^3 + 3(Al^2O^3, SiO^3) + 2CaO, SO^3$. |
| Hauyne from Niedermennig | $3NaO, SiO^3 + 3(Al^2O^3, SiO^3) + NaO, SO^3$. $2[3NaO, SiO^3 + (3Al^2O^3, SiO^3) + 2(CaO, SO^3)]$. |

*b*.—One part of mixture *a* is then intimately blended with one part of mixture *b*, and the powder closely pressed into an earthen crucible, so as to fill it completely. The crucible is then closed with a tight fitting cover, heated as rapidly as possible to a strong red heat by surrounding it with red-hot coals, and kept at that temperature for two hours. If the heat is raised too slowly, no liver of sulphur is formed, and the resulting mass is white, because most of the sulphur is volatilized; by a second ignition with carbonate of soda and sulphur, it may, however, be made to yield good ultramarine. After a successful ignition, the mass exhibits a greenish-yellow colour. It must now be gently ignited, with slight exposure to the air: *e. g.* in a covered porous crucible in which holes are made with a knitting needle. The blue mass thus obtained is reduced to powder, boiled with water, and well washed. (C. Gmelin, *Schw.* 54, 360.)

2. A mixture of equal parts of precipitated silica, carbonate of soda, and sulphur (all dry), is mixed with a quantity of solution of soda sufficient to dissolve the silica, the mixture pressed down into a crucible, which is rapidly heated to ignition, and kept at a strong red heat for an hour. The result is a bluish green mass, which, after subsequent roasting, assumes a beautiful blue colour. Porcelain clay from St. Yrieux, used instead of alumina in the second method, yields a less beautiful blue, because it contains iron; pipe-clay, a still less beautiful colour, because it contains a still larger amount of iron. (C. Gmelin.)

3. A mixture of 2 parts of porcelain clay, 3 parts of sulphur, and 3 parts of dry carbonate of soda, is gradually heated in a coated earthenware retort till it ceases to give off vapours; the retort is broken to pieces as soon as it is cold, and the green porous mass washed with water. The remaining blue powder is again heated to redness to expel the excess of sulphur. (Robiquet, *Ann. Pharm.* 10, 91.)

4. 1075 parts of crystallized carbonate of soda are fused in their own water of crystallization, and the fused mass mixed by stirring, first with 5 parts of red sulphide of arsenic—then with a quantity of hydrate of alumina, prepared from alum by precipitation with carbonate of soda, and containing 7 parts of anhydrous alumina—and lastly with a mixture of 100 parts of sifted clay and 221 parts of flowers of sulphur. The mass, after being intimately mixed and evaporated to dryness, is introduced into a crucible provided with a good cover, and gently heated at first, in order to expel the remaining traces of water, the temperature being afterwards raised to full redness. The mass should cake together without fusing. If the materials have not been properly mixed, the mass exhibits white spots; and if it has been fused, it is studded with brown spots. After cooling, it is roasted in order to expel the greater part of the sulphur; then reduced to powder and washed slightly on a filter with cold water. The bluish-green powder thus obtained, is again roasted for an hour or two, with occasional stirring, in covered basins, at a temperature never rising above low redness. (Tiremon, *Compt. rend.* 14, 761; also *J. pr. Chem.* 26, 314.)

A very small quantity of iron, such as is usually contained in the ingredients, is essential to the production of the colour, but excess is injurious. (Elsner, *J. pr. Chem.* 24, 384.) A mixture of one part of clay perfectly free from iron with one part of sulphur and 2 parts of anhydrous carbonate of soda, yields a yellowish mass when ignited; but if a trace of sulphate of iron is added to the mixture, a mass is obtained which is black, green, or blue, according to the degree of heat to which

it has been subjected. (Kressler, *J. pr. Chem.* 26, 106.) When potash is used instead of soda, the blue colour is not obtained. (C. Gmelin.)

Artificial ultramarine has a shade of green or grey, whereas the native compound inclines to a reddish tint. It sustains a low red heat without undergoing any change. When strongly ignited for a long time, it becomes dingy blue, and at last white. It is also decolorized by ignition in an atmosphere of hydrogen gas. (Elsner.) Hydrochloric acid destroys its colour, the change being attended with evolution of sulphuretted hydrogen and formation of a siliceous jelly. The silica after washing, contains, according to Elsner and Rammelsberg, a portion of sulphur mixed with it; whence it would appear, that a polysulphide of sodium (with sulphide of iron) is contained in ultramarine.

*Green ultramarine* appears to consist of artificial ultramarine which has not been roasted. When heated to redness, it becomes yellow, and afterwards, on cooling, greenish blue. (Elsner.)

¶ 5. Brunner (*Pogg.* 67, 541) recommends the following process: an intimate mixture is made of 70 parts of silica (he himself uses a peculiar sand found near Neugnau in Bern, and containing 94·25 per cent. of silica, 3·03 of alumina, 1·61 of lime, and 0·94 of sesquioxide of iron), 240 parts of burnt alum, 48 of powdered charcoal, 144 of flowers of sulphur, and 240 of anhydrous carbonate of soda, all previously reduced to an impalpable powder. The mixture is introduced into a hessian crucible, and the cover luted down. The crucible is then exposed to a moderate red heat kept as steady as possible for an hour and a half, after which it is suffered to cool. When the operation is successful, the mass presents a loose, semifused appearance, and a greenish or reddish-yellow liver of sulphur colour; it is also reduced to about two-fifths of its former volume. (If it appears solid, fused, browner in colour, and of still smaller bulk, we may conclude that the temperature has been raised too high.) The mass, which is readily detached from the crucible, is put into a dish and washed with either hot or cold water, till the liquid no longer has a sulphurous taste. The residual dark greenish-blue powder is then thrown on a filter and dried. The dry powder is next mixed with an equal weight of sulphur and 1½ times its weight of anhydrous carbonate of soda, and treated as before. The resulting mass, after washing and drying, is once more heated with the same proportions of sulphur and carbonate of soda, the product boiled for some time with water, and then thrown on a filter and washed with cold water, till the liquid which passes through ceases to affect acetate of lead. The powder after drying is passed through a fine sieve to separate impurities, and then treated in the following manner. A cast-iron plate or platinum dish is covered with a layer of pure sulphur, about one line in depth, and on this about the same quantity, or a little more, of the perfectly dry compound is sifted. The plate is then carefully heated till the sulphur takes fire, the compound itself, at the same time, being kept from ignition as much as possible. (Or the preparation may be mixed with half its weight of sulphur and cautiously heated as before.) This process is repeated three or four times, the residue on each occasion being detached from the plate and reduced to powder. The operation is repeated till a satisfactory colour is obtained.

Brunner is of opinion (1), that the presence of *lime* is accidental only, and of little consequence in the preparation of ultramarine;—(2), that the *iron* likewise plays but an unimportant part; since he has suc-

ceeded in preparing ultramarine with materials perfectly free from this metal; and (3), that the blue colour is dependent upon the soda, inasmuch as potash yields an analogous compound which is perfectly white. If the burning process with sulphur and carbonate of soda be continued after the compound has attained its finest colour, a point is reached at which it ceases to increase in weight; but if it be then heated without the addition of sulphur, an increase in weight is again observed, and a mass obtained having a paler blue colour with a tinge of black, resembling that of some varieties of native ultramarine. The powder at the same time loses its soft loose texture, and becomes denser and granular. In this state it does not evolve hydrosulphuric acid with hydrochloric acid, showing that it contains no unoxidized metallic sulphide.

Prückner adopts the following method. Sulphide of sodium, prepared by igniting the sulphate with powdered charcoal in a crucible or muffle, is dissolved in water; sulphur added to ensure saturation; the concentrated solution mixed with ½ per cent. of ferrous sulphate and 25 per cent. of well-prepared clay as pure as possible; the mixture evaporated to dryness; and the resulting mass reduced to powder and ignited for about an hour in a cupelling furnace. When cold, it is exhausted with water, dried, powdered, and once more exposed to heat in the muffle, whereby the desired colour is produced. It is ground down on a stone for use. (Prückner, *J. pr. Chem.* 33, 257.) ¶

| | *Natural Ultramarine.* | | | | *Artificial Ultramarine.* From Nuremberg. | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Clement & Désormes. | | C. Gmelin. | | *Blue.* Elsner. | | *Green.* Elsner. | | Varrentrapp. | | Brunner. | |
| KO | .... | | .... | | .... | | .... | | 1·75 | .. | | |
| NaO | 23·2 | .... | 12·06 | .... | 23·0 | .... | 25·5 | .... | 21·47 | Na | 16·91 | |
| CaO | 3·1 | (CaC) | 1·55 | .... | | .... | | .... | 0·02 | .... | 2·38 | |
| $Al^2O^3$ | 34·8 | .... | 22·00 | .... | 29·5 | .... | 30·0 | .... | 23·31 | .... | 25·25 | |
| $SiO^2$ | 35·8 | .... | 47·31 | .... | 40·0 | .... | 39·9 | .... | 45·60 | .... | 32·54 | |
| $SO^3$ | | .... | 4·68 | .... | 3·4 | .... | 0·4 | .... | 3·83 | .... | | |
| S | 3·1 | .... | 0·19 | .... | *a* 0·5 | .... | 3·6 | Cl | trace | .... | | |
| | | | | | *b* 3·5 | .... | 1·0 | S | 1·69 | .... | 11·63 | |
| FeO | | .... | | .... | 1·0 | .... | 0·9 | Fe | 1·06 | $Fe^2O^3$ | 2·25 | |
| HO ..... Resin, &c. | | .... | 12·21 | .... | | .... | | .... | | O | 9·04 | |
| | 100·0 | .... | 100·00 | .... | 100·9 | .... | 101·3 | .... | 98·73 | .... | 100·00 | |

S, *a*, in Elsner's analyses is sulphur evolved in the form of sulphuretted hydrogen when the mineral is treated with hydrochloric acid; S, *b*, is sulphur which remained attached to the silica. S, *a*, forms the largest proportion in the green (unroasted) ultramarine; the change from the green variety into the blue appears then to depend upon the abstraction of iron from the sulphide of iron, or of sodium from the protosulphide of sodium by the oxygen of the air and the formation of a sulphide of a higher degree of sulphuration. As the sulphur is more than sufficient to combine with the iron, sulphide of sodium must also be present, together with sulphide of iron. (Elsner.)

¶ F. Whrightson (*Ann. Pharm.* 54, 356) has analysed the two following silicates containing sulphuric acid.

| | *Dolerite.* | | *Semi-Opal,* of Shiffenberg. |
|---|---|---|---|
| KO | 1·83 | | 0·80 |
| NaO | 1·33 | | 0·90 |
| CaO | 9·89 | | |
| MgO | 6·66 | | 0·86 |
| $Al^2O^3$ | 6·14 | | 1·86 |
| FeO | 17·65 | | 4·11 |
| $SiO^2$ | 53·12 | | 90·20 |
| $SO^3$ | 0·86 | | 0·31 |
| HO | 1·93 | | 2·73 |
| | 99·41 | | 101·77 ¶ |

*d. Combination with Metallic Chlorides.*

1. *Sodalite.*—$3(NaO, SiO^2 + Al^2O^3, SiO^2) + NaCl$. Primary form: a rhombic dodecahedron; cleavage parallel to its faces; sp. gr. from 2·29 to 2·49; hardness equal to that of felspar. Transparent, white, grey, blue, &c. Fuses easily before the blowpipe, sometimes tranquilly, sometimes swelling up and forming a blistered glass. With hydrochloric acid it readily yields a siliceous jelly.

| | At. | *Sodalite.* | | Ekeberg. Greenland. | Arfvedson. Vesuvius. | Hoffmann. Ilmengebirge. |
|---|---|---|---|---|---|---|
| NaO | 4 | 124·8 | 25·35 | 25·00 | 26·23 | 24·47 |
| CaO | | | | | | 0·32 |
| $Fe^2O^3$ | | | | 0·15 | | |
| $Al^2O^3$ | 3 | 154·2 | 31·32 | 32·00 | 35·50 | 32·04 |
| $SiO^2$ | 6 | 186·0 | 37·77 | 36·00 | 33·75 | 38·40 |
| Cl − O | 1 | 27·4 | 5·56 | 6·75 | 5·30 | 5·48 |
| | 1 | 492·4 | 100·00 | 99·90 | 100·78 | 100·71 |

2. *Porcelain Spar.*—$4(CaO, SiO^2 + Al^2O^3, 2SiO^2) + NaCl$. Or, according to Schaffhäutl $4(Al^2O^3, SiO^3) + 2(CaO\ SiO^3) + (NaO, SiO^3) + \frac{1}{2}KCl$.—Rhombic prisms; $u^1 : u = 92°$ (nearly); cleavage parallel to *m* and *t*. Sp. gr. = 2·6. Softer than felspar. Transparent and colourless.—Fuses with tolerable facility, swelling up and forming a colourless blistered glass. Decomposed by strong acids, but without formation of a jelly. (Fuchs.)

| | At. | *Porcelain-spar.* | | Fuchs. | | Schaffhäutl. |
|---|---|---|---|---|---|---|
| NaO | | | | | | 6·5 |
| CaO | 4 | 112·0 | 14·97 | 15·25 | | 15·4 |
| $Al^2O^3$ | 4 | 205·6 | 27·48 | 27·50 | | 27·3 |
| $SiO^2$ | 12 | 372·0 | 49·72 | 49·42 | | 49·2 |
| NaCl | 1 | 58·6 | 7·83 | 7·83 | KCl | 1·2 |
| HO | | | | | | 1·2 |
| | 1 | 748·2 | 100·00 | 100·00 | | 100·8 |

*e. Combinations with Metallic Fluorides.*

*Lithia-mica, Lepidolite.*—Six-sided tables with two angles of about 122°, and four angles of 119°. Easily split into thin elastic laminæ, with metallic pearly lustre. Specific gravity from 2·8 to 3·0. Softer than calcspar. Transparent or translucent; biaxial to polarized light. —When heated it evolves water and hydrofluoric acid. Fuses very readily, swelling up and forming a glass which is for the most part transparent and colourless, but brown or black if it contains a larger quantity of iron. Colours the blowpipe flame-red, especially on the addition of bisulphate of potash. Dissolves readily and abundantly in borax, forming a transparent glass; dissolves in microcosmic salt, with the exception of a skeleton of silica, and forms a glass which becomes opalescent on cool-

ing; with carbonate of soda it fuses readily to a clear but somewhat blistered glass. In its natural state it is but imperfectly decomposed by acids, but after ignition, completely, without forming a siliceous jelly. —Lithia-mica contains : $1KO, 2LiO, 3Al^2O^3, 9SiO^2, 3F—O$. From this may be deduced the formula : $2(LiO, SiO^2) + 3(Al^2O^3, 2SiO^2) + (KF, SiF^2)$. The sesquioxides of iron and manganese partly replace the alumina.

| | At. | *Lithia-mica.* | | Turner, *a.* | Turner, *b.* |
|---|---|---|---|---|---|
| KO | 1 | 47·2 | 8·72 | 9·04 | 9·50 |
| NaO | | | | | |
| LiO | 2 | 28·8 | 5·32 | 5·49 | 5·67 |
| CaO | | | | | |
| $Mn^2O^3$ | | | | 1·23 | 1·08 |
| $Fe^2O^3$ | | | | | |
| $Al^2O^3$ | 3 | 154·2 | 28·48 | 28·30 | 28·77 |
| $SiO^2$ | 9 | 279·0 | 51·55 | 50·35 | 50·91 |
| F—O | 3 | 32·1 | 5·93 | 5·20 | 4·11 |
| Cl—O | | | | | |
| HO | | | | | |
| | 1 | 741·3 | 100·00 | 99·61 | 99·44 |

| | C. Gmelin. *c.* | Rosales. *d.* | Regnault. *e.* |
|---|---|---|---|
| KO | 4·90 | 10·96 | 8·79 |
| NaO | | 2·23 | |
| LiO | 4·21 | 2·77 | 4·15 |
| CaO | | 0·11 | |
| $Mn^2O^3$ | 4·57 | 4·30 | |
| $Fe^2O^3$ | 17·97 | | 13·22 |
| $Al^2O^3$ | 14·14 | 20·80 | 19·88 |
| $SiO^2$ | 46·23 | 48·92 | 49·78 |
| F—O | 8·53 | 5·97 | 4·24 |
| Cl—O | | 1·02 | |
| HO | 0·83 | | |
| | 101·38 | 97·08 | 100·06 |

*a*, is Lithia-mica from the Ural;—*b*, Lepidolite from Utön; *c*, Lithia-mica from Zinnwald;—*d*, from Mursinsk, in the Ural;—*e*, a brownish yellow variety of unknown origin.

*Combination of a Silicate with Aluminate of Magnesia.—Xanthophyllite*, with which also *Seybertite*, *Holmesite* or *Chrysophane* appear to be identical.—$1CaO, 2MgO, 2Al^2O^3, 1SiO^2, 1Aq = 2(MgO, Al^2O^3) + CaO, SiO^2 + Aq$.—Occurs in tables which have a plane of cleavage parallel to the principal face. Sp. gr. from 3·0 to 3·1. Hardness equal to that of apatite.

| | At. | *Xanthophyllite.* | | Meitzendorf, *a.* | Plattner. *b.* | Clemson. *c.* |
|---|---|---|---|---|---|---|
| NaO | | | | 0·61 | trace | |
| CaO | 12 | 336·0 | 13·14 | 13·26 | 12·5 | 10·7 |
| MgO | 24 | 480·0 | 18·78 | 19·31 | 9·8 | 24·3 |
| FeO | | | | 2·53 | | 5·0 |
| $Fe^2O^3$ | 1 | 78·4 | 3·07 | | 4·3 | |
| $Al^2O^3$ | 23 | 1182·2 | 46·24 | 43·95 | 46·7 | 37·6 |
| $SiO^2$ | 12 | 372·0 | 14·55 | 16·30 | 16·4 | 17·0 |
| HO | 12 | 108·0 | 4·22 | 4·33 | 3·5 | 3·6 |
| | 1 | 2556·6 | 100·00 | 100·29 | 93·2 | 98·2 |

*a*, is Xanthophyllite from Siberia; *b*, and *c*, Seybertite from Amity in the State of New York.

## Silicium and Thorinum.

Silicate of Thorina.—*Thorite.* Before the blowpipe this mineral assumes a brownish red colour without fusing. It is decomposed by hydrochloric acid with formation of a jelly. Contains in 100 parts: KO 0·24, NaO 0·10, CaO 2·58, MgO 0·36, PbO 0·80, $Mn^2O^3$ 2·39, $Fe^2O^3$ 3·40, $Al^2O^3$ 0·06, $U^2O^3$ 1·61, $SnO^2$ 0·01, ThO 57·91, $SiO^2$ 18·98, HO 9·50. (Undecomposed mineral, 1·70; loss, 0·49.) (Berzelius.)

## Silicium and Zirconium.

A. Silicate of Zirconia.—*Zircon, Hyacinth.*—$2ZrO, SiO^2$.—Crystalline system the square prismatic. *Fig.* 29, 30, and other forms. $e : e = 124° 12'$; $e : q = 117° 48'$; $e : r = 131° 49'$; cleavage parallel to $r$. (Hauy.) Sp. gr. from 4·4 to 4·5. Harder than quartz.—Does not fuse before the blowpipe, although it loses colour. In a large quantity of borax it dissolves with difficulty, and forms a transparent glass; with a smaller quantity it forms a turbid glass; does not dissolve to any perceptible extent in microcosmic salt or carbonate of soda. Not decomposed by acids—even by hydrofluoric acid—hot oil of vitriol, however, acts slightly on it. (Berzelius.)—When chlorine gas is passed over an ignited mixture of powdered zircon and charcoal, chloride of silicium is alone evolved, and the residual mass gives up no zirconia either to water or to hydrochloric acid. (Wöhler, *Pogg.* 11, 148.) Zircon may be fused with potash, lime, or oxide of lead.

| | At. | *Zircon.* | | Berzelius. Auvergne. | Klaproth. Norway. | Vauquelin. Ceylon. |
|---|---|---|---|---|---|---|
| ZrO | 2 | 60·8 | 66·23 | 67·16 | 65 | 64·5 |
| $SiO^2$ | 1 | 31·0 | 33·77 | 33·48 | 33 | 32·6 |
| $Fe^2O^3$ | | | | | 1 | 2·0 |
| | 1 | 91·8 | 100·00 | 100·64 | 99 | 99·1 |

B. Fluoride of Silicium and Zirconium.—White, pearly crystals, very soluble in water. The solution becomes turbid on boiling; but the greater part of the salt remains dissolved. (Berzelius.)

C. Silicate of Zirconia and Potash.—One part of powdered zircon is ignited for some time with from two to four parts of hydrate of potash in a silver crucible, and the cooled mass exhausted with water, which takes up the excess of potash, together with a small portion of silica, leaving the double silicate of zirconia and potash in the form of an insoluble powder. In pure water this salt remains suspended for a considerable time, but from water containing potash it is soon deposited. It is perfectly soluble in dilute hydrochloric acid. (Chevreul.) If 400 parts of hydrate of potash are used to every 100 parts of zircon, the water extracts 5 per cent. out of the 33 per cent. of silica contained in the zircon, together with the excess of potash; and the washed residue, after ignition, weighs 125 parts; it therefore contains 30 parts of potash. (Berthier, *Ann. Chim. Phys.* 59, 193.)

D. Silicate of Zirconia and Lime.—Prepared by fusing a mixture of zircon with quartz and marble in various proportions, in a charcoal

crucible exposed to the heat of a blast furnace. By this means the iron in the zircon is reduced.—*a*. 100 parts of zircon with 234 parts of quartz and 333 parts of marble yield a dense transparent glass surrounded with a white stony crust.—*b*. 100 : 101 : 333; pulverulent, slightly baked together.—*c*. 100 : 267 : 222; imperfectly vitrified, white opaque, resembling porcelain.—*d*. 100 : 334 : 222. Light grey, transparent glass, with conchoidal fracture.—*e*. 100 : 167 : 222; merely softened; pale grey, with granulated fracture.—*f*. 100 : 100 : 111; perfectly fused, semi-vitreous, dense.—*g*. 100 : 67 : 111; sometimes opaque and stony; sometimes transparent and vitreous, with conchoidal fracture and diamond lustre.—*h*. 100 : 33 : 111; white, opaque, with shining and somewhat laminated fracture.—*i*. 100 : 16 : 111; white opaque, dull, and stony. Those of the above mixtures in which the lime amounts to less than one-third, are decomposed by acids. (Berthier, *Ann. Chim. Phys.* 59, 190.)

The following minerals, though belonging to this head, do not admit of accurate calculation :—

*Eudialite.*—Crystalline system the rhombohedral. Primary form, an acute rhombohedron, *Fig.* 151, $r^3 : r^3 = 73° 40'$; cleavage parallel to *p*. Specific gravity = 2·89. Harder than apatite. Translucent and of a reddish colour. Before the blowpipe it fuses with tolerable facility to a greyish-green enamel. Dissolves readily in borax, yielding a glass slightly coloured by iron. Easily decomposed by microcosmic salt, the skeleton of silica swelling up to such an extent as to destroy the globular form of the bead. With carbonate of soda it forms a very refractory glass. (Berzelius.) It is completely decomposed by hydrochloric acid with formation of a jelly.

*Oerstedtite.*—Crystalline system the square prismatic, with three square-based octohedrons and two square prisms; the angles very nearly agree with those of zircon. Specific gravity = 3·629. Harder than apatite. Evolves water when heated. Infusible before the blowpipe. With borax or microcosmic salt, it yields a colourless glass. Does not dissolve in carbonate of soda. (Forchhammer.)

| | *Eudialite.* Stromeyer. | | | *Oerstedtite.* Forchhammer. |
|---|---|---|---|---|
| NaO | 13·82 | CaO | | 2·61 |
| CaO | 9·79 | MgO | | 2·05 |
| ZrO | 11·10 | FeO | | 1·14 |
| $Mn^2O^3$ | 2·06 | $ZrO + TiO^2$ | | 68·96 |
| $Fe^2O^3$ | 6·75 | $SiO^2$ | | 19·71 |
| $SiO^2$ | 53·33 | HO | | 5·53 |
| HO | 1·80 | | | |
| Cl—O | 1·03 | | | |
| | 99·68 | | | 100·00 |

¶ [For an extensive and interesting arrangement of polymeric-isomorphous minerals, chiefly comprising those of the talc genus, *vide* Th. Scheerer, *Pogg.* 71, 445; also Berzelius, *On the Formation of a Scientific System of Mineralogy*, *Pogg.* 71, 456.]

The discoveries of Ebelmen, relating to the artificial formation of minerals, may be appropriately introduced in this place. By fusing together a mixture of alumina and magnesia in the same proportions as they exist in spinelle—with boracic acid (as a flux)—in the strongest

heat of a pottery-furnace, Ebelmen obtained a great number of regular octohedrons mixed with dodecahedrons, which were perfectly infusible before the blowpipe, and scratched glass. By adding a small quantity of chromic oxide or oxide of cobalt, the crystals were obtained of a red or blue colour. The specific gravity of the crystals varied from 3·52 to 3·58. Again, by igniting a mixture of alumina and yttria (or glucina ?), in the proportions of Cymophane, with boracic acid, a crystalline mass is obtained which scratches topaz. Alumina may be obtained in the crystalline form, by fusing a mixture of one part of alumina with between 3 and 4 parts of fused borax. (*Compt. rend.* 25, 661.) In a subsequent paper, Ebelmen gives the method of proceeding and the proportions as follows :—For red spinelle, 6 parts of alumina, 3 parts of magnesia, 6 parts of fused boracic acid, and from ·10 to ·15 parts of chromic oxide; and for the blue crystals, the same proportions, substituting oxide of cobalt for the chromic oxide. The substances, after being weighed out separately, are intimately mixed and put into a broad, flat-bottomed dish of unglazed porcelain, lined with platinum foil. The dish is then placed in a protecting crucible similar to that used in the manufacture of porcelain, but smaller; and the whole exposed in a pottery furnace (such as that of Sèvres), and left there during the regular period of burning. (*Ann. Chim. Phys.* 22, 213.)

### Other Compounds of Silicium.

With tin, lead, iron, copper, silver, and platinum.

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## Chapter XVI.

# TITANIUM.

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Gregor. *Crell. Ann.* 1791, 1, 40, and 103.
Klaproth. *Beiträge*, 1, 223, 245; 2, 222, and 226; 4, 153.
Lowitz. *Crell. Ann.* 1799, 1, 183.
Richter. *Ueber d. n. Gegenst. d. Chem.* 10, 104.
Lampadius. *Samml. prakt. Chem. Abhandl.* 2, 113; also *Crell. Ann.* 1796, 1, 259.
Vauquelin & Hecht. *Journal des Mines*, 15, 20.
Vauquelin. *Ann. du Muséum d'Hist. Nat.* E. 6, p. 93; also *A. Gehl.* 5, 464;—Further, *J. Phys.* 66, 345.
Laugier. *Ann. Chim.* 89; 306; also *Schw.* 19, 54.
Wollaston. *Phil. Transact.* 1823, 17 and 400; also *Schw.* 41, 83, and 42, 236; also *Gilb.* 75, 220.
H. Rose. *Gilb.* 73, 67, and 129;—*Pogg.* 3, 163; 12, 492; 15, 145; 16, 57; 24, 141; 42, 527.

SYNONYMES : *Menakan, Titan Titane.*

*History.*—Oxide of titanium, already made known by Gregor in 1791 as a new metallic oxide occurring in Menakite, was found also in Rutile in 1794 by Klaproth, who more accurately investigated the chemical properties of titanium; this metal was still further examined in 1821 by H. Rose.

*Sources.*—As free titanic acid in Rutile and Anatase; as titanic acid combined with various oxides in Titanite, Titaniferous iron, Berowskite, Greenovite, Mosandrite, Euxenite, Aeschinite, Polymignite, Oerstedtite; as fluoride of titanium in Warwickite; as titanic acid or a titanate, in very minute quantities and accidentally, in the Quartz of Rabenstein and in the Corundum of Piedmont (Fuchs), in many varieties of Mica (Peschier), in Chrysoberyl (Segbert), in Acmite (Von Kobell), in Pyrochlore (Wöhler), and in the clay of Cracow and Freiberg (Kersten). According to Brett and Bird (*Pogg.* 34, 518), hessian crucibles contain from 1 to 30 per cent. of titanic acid; but Wöhler and Schwarzenberg (*Pogg.* 35, 507), Erdmann (*J. pr. Chem.* 4, 496), and Herberger (*Rpeert.* 55, 62), could not discover any titanium in them. In a similar manner, Marchand (*J. pr. Chem.* 16, 372) refuted the assertion of Rees (*Phil. Mag. J.* 5, 398, and 6, 201), who states that the suprarenal glands and the blood of man contain titanium.

*Preparation.*—1. When titaniferous iron ores are fused in iron smelting furnaces, the titanium likewise separates in the metallic state, and is found in very small cubical crystals, both in the slag and in the iron which collects in cavities in the hearth, and is broken up when the stone work is renewed. By dissolving out the iron with boiling hydrochloric acid, treating the residue with aqua-regia, then washing away the graphite, and lastly separating by mechanical means those portions of the slag which are left undissolved by hydrochloric acid, the crystals of titanium are obtained in a state of purity. The mass may also be repeatedly boiled with dilute sulphuric acid, then with aqua-regia to dissolve the ferrous silicate, and afterwards washed with water—the pieces of carbon being crushed with a cork and washed away. The larger fragments of silica are then to be picked out, and the smaller ones removed by fusion with carbonate of potash and digestion in water; the residue is pure titanium. (A. Werner, *J. pr. Chem.* 16, 212.) Wollaston discovered these crystals of titanium in the iron-slags of Merthyr Tydvil in Wales; they had also been previously found—though their real nature was not recognized—in the slags of the iron-works of Low Moor in Yorkshire, of Pidding in Derbyshire, of Pontypool in Monmouthshire, and of Clyde in Scotland. Recently, they have been remarked by Nöggerath (*Kastn. Arch.* 4, 351), Meyer (*Kastn. Arch.* 13, 272), and Hünefeld (*Schw.* 50, 332), in the slag of the Royal Works of Upper Silesia; by Karsten (*Pogg.* 3, 175) in a Silesian blast-furnace; by Walchner (*Schw.* 41, 80; 44, 47) in the iron on the hearth of a blast-furnace at Kandern, in the Oberland of Baden; by Zinken (*Pogg.* 3, 175) in the blast-furnace at Mägdesprung in the Hartz; by Laugier (*Bull. Phil.* 1825, 102) in a blast-furnace in the department of the Moselle; and by Karl Stumm, in a similar manner, in the blast-furnaces of Fischbach, Bettingen, and Abentheuer near Saarbrücken. The specimen found in a

collection by Nöggerath (*Schw.* 65, 385), six ounces in weight, and consisting of three-fourths of crude titanium to one fourth of pig-iron—appears likewise to have been obtained from one of these iron-works. Blumenau (*Ann. Pharm.* 67, 122) describes a specimen of titanium found in a smelting-furnace at Rübeland in the Hartz, the weight of which was at least 80 lbs.

2. Oxide of titanium is mixed with oil or a small quantity of charcoal, and exposed in a covered crucible to the strongest heat of a blast-furnace. (Vauquelin, Lampadius, Laugier.) The reduction or at least the fusion of the reduced metal is but very imperfectly effected. Faraday (*Gilb.* 66, 188) did not succeed in fusing it in a blast-furnace in which Hessian crucibles were melted. Berthier exposed a mixture of one part of rutile, one part of dry carbonate of soda, one part of sulphur, and rather more than one-fifth part of charcoal, in a black-lead crucible lined with charcoal, to the strongest heat he could produce, for the space of two hours; and obtained a mixture of titanium crystallized in cubes with sulphide of titanium and a compound of titanous oxide and soda. The latter he separated by treating the mass first with water and then with cold oil of vitriol, after which he removed the sulphide of titanium by elutriation. If the ignition is continued for a shorter time only, the product contains a smaller quantity of titanium and a larger quantity of the sulphide

*The reduction of the metal in a charcoal crucible* is generally accomplished in the following manner:—

For the fusion either an assay crucible (of the form of a cup) is used, or an ordinary crucible attached to a support of burnt clay by a luting of moist clay. The vessel must be made either of Hessian or some other very refractory clay. Either a thick layer of lamp-black or charcoal powder moistened with water, paste, or oil, is pressed round the the bottom and sides of the crucible; or the crucible is filled with a stiff paste of charcoal powder and thin clay, and when this paste is dry, a cylindrical hole reaching nearly to the bottom is bored in the middle of it with a knife: this hole is called the *bore*.

The metallic oxide is either introduced into the cavity alone; or it is previously made into a thick paste with oil, by which means its volume is reduced; or lastly it is mixed with charcoal or lamp-black besides the oil. The quantity of charcoal should not amount at most to more than sufficient to convert half the oxygen of the oxide into carbonic oxide (therefore, about 3 parts of charcoal to every 8 parts of oxygen in the oxide); for since the sides of the charcoal crucible likewise absorb oxygen from the metallic oxide, a portion of combined charcoal may remain in the mixture, and by its intervention prevent the reduced metal from uniting into a solid mass—the regulus or button. The reduction is, however, more rapidly effected with a moderate addition of charcoal than when the lined crucible is alone employed. Formerly a flux was added to the oxide of titanium, such as borax, glass, &c. This addition certainly facilitates the union of the reduced metal into a button, but at the same time may cause it to be contaminated with sodium, silicium, &c. After the oxide of titanium has been strongly compressed into the bore, the upper part of the crucible is filled with powdered charcoal or lamp-black closely pressed down, and the cover luted on with clay. It is then placed in a blast-furnace,—Seftstrom's for instance (*Pogg.* 15, 612) or Mohr's (*Ann. Pharm.* 27, 229); heated to redness very gradually, so as to prevent cracking; and afterwards kept at a white heat for half an hour

or more; fresh fuel, consisting either of small pieces of charcoal or of coke being frequently added—so that the crucible may be constantly surrounded with ignited material—and the fire frequently stirred with a poker, lest an empty space should be formed in the furnace and cause the crucible to fall over. The fire is then allowed to burn down without stopping the blast, till the crucible can be laid hold of with the tongs. The blowing is then discontinued, and the crucible carefully taken out before the slag by which it is attached to the furnace has had time to solidify; it is then left to cool slowly.

3. When a mixture of potassium and anhydrous fluoride of titanium and potassium is heated, the titanium is set free with vivid incandescence; the fluoride of potassium may then be removed by digestion in water. (Berzelius.)

4. When chloride of titanium and ammonium is sublimed in a glass tube or flask, the titanium remains behind in thin scales. (H. Rose.) Liebig (*Pogg.* 21, 259) half fills a glass tube three feet long and half an inch in diameter, quite loosely with the double chloride of titanium and ammonium; lays it horizontally in a furnace; passes a continuous current of ammoniacal gas through it; then heats the empty part first; and gradually extends the fire to the other extremity till the glass becomes soft. The colder end of the tube is kept free from the condensed chloride of ammonium, which might otherwise stop it up, by means of a small glass rod. The titanium is completely reduced, but must not be removed from the tube till the whole has become cold, as otherwise it will take fire.

5. A mixture of sodium and ammonio-chloride of titanium is rubbed to powder during winter in an agate mortar, but without strong pressure. Should any part of it take fire, the combustion may be prevented from extending by covering the burning portion with a fresh quantity of the ammonio-chloride. The mixture is then introduced as quickly as possible into a capacious, long-necked glass flask; the stopper —through which a glass tube bent at right angles passes—immediately inserted, and heat applied by means of an argand spirit-lamp. Reduction takes place, accompanied by a violet light and formation of a slight cloud of metallic titanium, a portion of which is projected from the vessel. Part of the ammonio-chloride of titanium likewise sublimes in its original state. The mass when cold is treated with water containing hydrochloric acid, and the black titanium-powder is thrown on a filter and washed with water, to which a constantly decreasing proportion of hydrochloric acid is added. If pure water is used, the finely divided metal passes through the filter. (H. Rose.)

Clarke states that he has obtained from oxide of titanium before the oxy-hydrogen blowpipe, a silver-white metallic globule.

*Properties.* Titanium, as obtained by the first method, has the form of very small cubes, whose faces often exhibit step-like indentations. (Wollaston.) Cleavage parallel to the faces of the cube (W. Phillips), and likewise to those of a rhombic dodecahedron (Walchner); parallel to the faces of an octohedron, and less distinctly parallel to those of the cube (Nöggerath). Specific gravity = 5·28 (Karsten); 5·3 (Wollaston). Scratches steel and rock-crystal. (Wollaston.) Very brittle. Of a yellowish copper colour and high metallic lustre. (Wollaston.) Difficult to powder; when pounded it exhibits a reddish yellow colour. (Walchner.) Fuses only at the most intense white heat. Zinken's statement (*Pogg.* 28, 160), that titanium is volatilized at the heat of a powerful blast-furnace,

requires confirmation. Titanium is a very good conductor of electricity; when it retains a trace of iron, it is slightly magnetic, but not otherwise. (Wollaston.) Titanium prepared by the second method is generally pulverulent; according to Vauquelin and Lampadius, it is copper-coloured, but according to Laugier, golden yellow; Berthier obtained it in copper-coloured cubes.—That prepared by the third method has the form of a black powder, which under the burnishing steel assumes the metallic lustre. (Berzelius.)—Titanium, as obtained by the fourth method, has the form of a dark violet-blue powder, or of cohering scales exhibiting a coppery lustre. (Liebig.) That portion of the metal which adheres in a fine film to the glass, reflects light of a red colour and transmits it green. (H. Rose.)—The titanium prepared by the fifth method takes the form of a bluish black powder, which by pressure acquires metallic lustre and the colour of copper. (H. Rose.) ¶ Berzelius distinguishes two allotropic modifications of titanium, which he calls respectively *Ti α* and *Ti β*; *Ti α*—prepared by Rose's method from bichloride of titanium by means of ammonia, takes fire when heated in the air and burns vividly, yielding titanic acid; it is oxidized by boiling nitric acid, and readily dissolved by aqua-regia. *Ti β*, on the contrary, which is the modification obtained by the ordinary methods, is well known to resist the action of heat and strong acids. ¶

*Atomic weight of titanium:* 24·295 (H. Rose); 23·665 (Mosander); the mean being about 24. ¶ 314·7 or 25·17 (Pierre, *Ann. Chim. Phys.* 3, 20, 257). ¶

## *Compounds of Titanium.*

### Titanium and Oxygen.

### A. Titanous Oxide.

The following experiments render probable the existence of an oxide of titanium containing less oxygen than titanic acid.

If titanic acid made into a paste with oil is exposed in a charcoal crucible for six hours to the heat of a blast-furnace, the outside appears covered with a brown crust; within this is a stratum full of cavities containing gold-coloured particles, probably consisting of metallic titanium; and in the centre is a denser mass composed of small, bluish-black, shining needles [probably titanous oxide]. (Laugier.)

When titanic acid, unmixed with any carbonaceous matter, is strongly ignited in a charcoal crucible, the mass becomes coated externally with a crystalline, copper-coloured crust of titanium; but in the interior there is formed a black substance, producing a grey and somewhat brilliant streak, not dissolved by any acid, even by a mixture of hydrofluoric and nitric acids; very slowly oxidized when ignited in the air, and scarcely even by fusion with nitre; and lastly, dissolving in microcosmic salt before the blowpipe to a black, dark red, or hyacinth-coloured glass. (Berzelius.)

Titanic acid heated to whiteness in a charcoal crucible by itself, loses only 5 or 6 per cent. of oxygen; the resulting black mass is probably, therefore, a mixture of titanic acid with titanous oxide. It imparts an amethyst colour to glass, and forms wine-red solutions with the stronger acids, but not with acetic acid. From these solutions ammonia precipitates a beautiful blue, gelatinous hydrate, which, however, is rapidly decomposed by the water at ordinary temperatures, and converted into

white titanic acid. When titanic acid mixed with 12 per cent. of charcoal, is strongly ignited in a charcoal crucible, it loses from 13 to 16 per cent. of oxygen, and is converted into a yellowish brown, granular, very friable mass, having a metallic lustre. With 24 per cent. of charcoal the titanic acid loses at most 20 per cent. of oxygen, and leaves a cake coloured black by admixture of charcoal.—In these experiments with charcoal, titanous oxide is probably formed, surrounded with metallic titanium. (Berthier, *Ann. Chim. Phys.* 50, 374.)

When titanic acid is ignited with filings of purified zinc in a covered crucible till the latter passes off in vapour, and the rest of the zinc separated by means of hydrochloric acid, the titanic acid remains unchanged in weight, in the form of a black powder, which, when ignited in the air, becomes white again without increase of weight. (H. Rose.)

In the above experiment of Rose, a black powder is obtained if the temperature is raised only to low redness; but if one part of titanic acid is introduced with 10 parts of zinc into a glass flask, the neck of which is drawn out to a small diameter, and the vessel is then heated in an earthen crucible filled up with sand, till all the zinc is sublimed, the residue, after being treated with hydrochloric acid, yields a deep indigo-blue powder. A dirty blue powder is likewise obtained, when vapour of zinc is passed over titanic acid (or acid titanate of soda), ignited in a porcelain tube, and the greenish-blue mass is freed from zinc and cadmium by digestion in hydrochloric acid. The blue powder, when ignited in oxygen gas, increases somewhat in weight, and assumes a dark yellow colour which becomes paler on cooling; after this treatment, hydrochloric acid dissolves out fresh portions of zinc and cadmium. (Kersten, *Pogg.* 50, 313; also *J. pr. Chem.* 20, 373.)

Clay containing titanic acid is turned blue by ignition with de-oxidizing substances. Muffles made of the titaniferous clay of Cracow, which have been used for the distillation of zinc, become partially vitrefied, and then assume a beautiful violet blue-colour. Meissner porcelain-clay made into a pasty mass with oxide of zinc, charcoal, sugar, and water, and ignited first gently and afterwards strongly in a crucible with the cover luted down, sometimes acquires a light blue colour, and sometimes becomes black from admixture of charcoal; but in the latter case it may be turned blue by gentle ignition in the air. The clay does not acquire a blue colour without the addition of oxide of zinc. The mixture of titaniferous marl and coke-dust in the hearths of the Freiburg blast-furnaces exhibits a lavender-blue colour at the end of the smelting process. (Karsten.)

Many fluxes, in which titanic acid is dissolved, are coloured violet-blue by deoxidizing agents:—*e. g.*, borax or microcosmic salt, by the action of the interior blowpipe-flame. (Berzelius.)

A mixture of potash or soda glass with titanic acid, fused in a crucible the sides of which are covered with zinc, or a mixture of oxide of zinc and charcoal, yields either a black or a dingy violet-coloured glass. A mixture of silica, alumina, lime, and 5 per cent. of titanic acid, similarly treated with zinc, gives a lavender-blue—and with tin instead of zinc, a beautiful blue enamel; with 10 per cent. of titanic acid, the colour is deeper; a powerful heat and the total exclusion of atmospheric air, are necessary for the success of this operation. (Karsten.) The blue colour of many slags is also due to the presence of titanous oxide. (Berthier.) The blue colour of many of these slags, however, is not caused by titanium, but by their conversion into Reaumur's porcelain. (Fournet.) [Vid. III., 385.]

Zinc, tin, and iron, and likewise copper, when aided by heat, first impart a violet or red colour to the solution of titanic oxide in various acids, and then precipitate a powder of the same colour, possibly consisting of titanous oxide combined with oxide of zinc, &c. The same precipitate is obtained on adding an alkali to the solution coloured by the above-mentioned metals. But whether obtained by the slow action of these metals, or by the addition of an alkali, it is soon converted into white titanic acid, sometimes by the action of the air, sometimes when the air is excluded (according to H. Rose and Berthier), by the decomposition of water. By a careful addition of alkali, according to Berthier, white titanic acid is first precipitated, and then the coloured titanous oxide.

¶ *Sesquioxide of Titanium.*—When anhydrous titanic acid is very strongly ignited in a current of dry hydrogen gas, it becomes black and loses considerably in weight. From a determination of the actual loss of weight, Ebelmen concludes that sesquioxide of titanium is produced. The residue is not acted on by nitric or by hydrochloric acid, but dissolves in sulphuric acid, forming a violet-coloured solution. (Ebelmen, *Ann. Chim. Phys.* 20, 385.) ¶

## B. Titanic Oxide or Titanic Acid, $TiO^2$.

*Binoxide of Titanium, Oxyde de Titane.*—Found native as *Rutile* and *Anatase.*

*Formation.* The metal prepared by the first method undergoes no alteration in the air, at ordinary temperatures; at a red heat it is slowly oxidized, first becoming black, and ultimately changing into the white oxide. (Wollaston.) The metallic laminæ obtained by the fourth method burn when heated in the air, and form titanic acid (H. Rose, Liebig); the powder obtained by the fifth method burns with still greater facility. (H. Rose.) The metal prepared by the first method is superficially oxidized by nitre at a red heat, and acquires a purple or blue colour; borax and carbonate of soda act only in proportion to the tendency of the metal itself to oxidize in the air. The addition of nitre as an oxidizing agent to borax, together with a small quantity of carbonate of soda to promote the union of the borax with the nitre, causes the titanium to dissolve rapidly in the borax in the form of titanic acid; from the fused mass, water separates a white powder (acid titanate of soda) which is soluble in acids. (Wollaston.) Titanium exposed at a red heat to a current of steam, is converted, with rapid disengagement of hydrogen gas, into titanic acid. (Regnault, *Ann. Chim. Phys.* 62, 355.) Titanium prepared by the first method is neither dissolved nor oxidized by sulphuric, hydrochloric, hydrofluoric, nitric, or nitro-hydrochloric acid, not even at the boiling points of these liquids (Wollaston); but it dissolves in a hot mixture of nitric and hydrofluoric acids. (Berzelius.) The metal obtained by the fourth method is not soluble in hydrochloric acid, and dissolves with great difficulty in hot nitric acid, but more readily in aqua-regia; that prepared by the fifth method dissolves with greater facility. (H. Rose.)

*Preparation.* The substances from which titanic acid is extracted, are rutile (titanic acid, contaminated with ferric oxide, and manganic oxide, and sometimes also with stannic oxide, silica, and alumina) and titaniferous iron (titanate of ferrous oxide). The latter may be freed from the greater part of the iron by repeated boiling with fresh quantities of hydrochloric acid.

1. One part of powdered rutile or titaniferous iron, after digestion in hydrochloric acid, is fused with 2 parts of hydrate of potash in a silver crucible (Laugier), or with 3 parts of carbonate of potash (H. Rose), in a platinum, silver, black-lead, charcoal, or earthen crucible. The mass is then digested with cold water, and the insoluble acid titanate of potash, contaminated with sesquioxide of iron, is washed with the same liquid till it begins to pass through the filter and render the wash-water milky. The solution contains the excess of potash in combination with manganic acid, stannic acid, silica, alumina, and a trace of titanic acid; as soon as the water ceases to contain any considerable quantity of free potash, the acid titanate of potash is carried with it through the filter. For the separation of the sesquioxide of iron, the following methods are employed:

*a.* The washed residue is dissolved in cold concentrated hydrochloric acid—an operation which takes a long time—and the solution, diluted with water, filtered, and heated to the boiling-point—the more complete precipitation of the oxide of titanium being promoted by the addition of oxalic acid or oxalate of ammonia. Lastly, the precipitate is well washed and ignited. (Laugier.) Instead of oxalic acid, sulphuric acid may also be used. In either case, however, the oxide of titanium carries down with it a portion of ferric oxide, by which, after ignition, it is slightly tinged with yellow even when cold. (H. Rose.)

*b.* The solution of the washed precipitate in concentrated hydrochloric acid is diluted with water, filtered, and kept in a state of ebullition for a considerable time—by which means nearly all the titanic acid (mixed with iron and manganese) is precipitated. The precipitate, while still hot, is thrown upon a filter, and washed with boiling water acidulated with hydrochloric acid; because when washed it with pure water, especially if cold, it runs through the filter. The acidulated water dissolves a small quantity of the oxide; but it may be recovered by evaporating the liquid. To free the washed titanic oxide from all traces of oxide of iron, it is dissolved, while freshly precipitated, in strong hydrochloric acid, and again precipitated by dilution in water and boiling. It is then washed with boiling water acidulated with hydrochloric acid, and the same operations repeated five or six times, till a portion of the titanic oxide thus obtained exhibits a snowy whiteness after ignition and cooling. A considerable quantity of titanic oxide remains in the acid filtrates; but it may be recovered by precipitation. (H. Rose.)

*c.* The hydrochloric acid solution of the washed residue is precipitated by ammonia, and the washed precipitate, consisting of titanic acid chemically combined with the oxides of iron and manganese, is digested with hydrosulphate of ammonia, which dissolves any oxide of tin that may be present, and converts the sesquioxides of iron and manganese into hydrosulphates of the protoxides, which are then removed by hydrochloric acid, the titanic acid being left behind in a state of purity. (H. Rose.)

*d.* The hydrochloric acid solution is mixed with tartaric acid and water; supersaturated with ammonia—which, when a sufficient quantity of tartaric acid is added, produces no precipitate; the iron and manganese precipitated by hydrosulphate of ammonia; the solution filtered and evaporated to dryness; and the residue ignited under a muffle; the pure oxide then remains behind. The oxide of titanium obtained by this process may be contaminated with lime, since commercial tartaric acid contains a portion of that substance. (H. Rose.)

*e.* The washed residue is dissolved in cold hydrochloric acid of medium strength; the solution diluted with a very large quantity of water; then

saturated with hydrosulphuric acid; filtered, in case any precipitate of sulphide of tin is formed; and the titanic acid, together with hydrosulphate of ferrous oxide, precipitated from the filtrate in a close vessel by ammonia. The whole is then allowed to settle quietly; the clear liquid decanted off; the precipitate treated with an aqueous solution of sulphurous acid in excess, to dissolve the ferrous hydrosulphate; and the insoluble residue of titanic acid lastly washed and ignited. (Berthier, *Ann. Chim. Phys.* 50, 362; also *Ann. Pharm.* 5, 246.)

*f.* The hydrochloric acid solution of the titanic acid containing sesquioxide of iron, is boiled with an excess of sulphide of ammonium as long as the precipitate first formed continues to increase. It is then filtered and washed, out of contact of air, to prevent the iron from becoming oxidized and thereby precipitated. The whole of the iron remains dissolved in the liquid, in the form of protoxide; but every trace of the titanic oxide is precipitated. (Berthier, *N. Ann. Chim. Phys.* 7, 85.)

2. Hydrosulphuric acid gas is passed over finely pounded titaniferous iron or rutile strongly ignited in a porcelain tube, as long as water continues to be formed. The resulting mixture of titanic acid and sulphide of iron is digested with concentrated hydrochloric acid, which dissolves the iron with disengagement of hydrosulphuric acid and precipitation of sulphur; and the remaining titanic acid is washed with water and ignited. As it still, however, retains a portion of iron, and consequently exhibits a reddish colour, the same process is once more repeated; it is then obtained perfectly white and pure. Ferruginous titanic acid may always be purified in this manner. If the porcelain tube is not ignited very strongly, the titanic acid which is obtained passes through the filter on being washed. A better process, however, is the following: The purified titaniferous iron is fused in a hessian crucible with sulphur, and the resulting mixture of titanic acid, sulphide of iron, and sesquioxide of iron (from the action of air) is treated with hydrochloric acid. The titanic acid, which is still red from the presence of iron, is washed and ignited, and lastly heated to redness in a porcelain tube, and subjected to the action of hydrosulphuric acid as above. (H. Rose.)

3. A mixture of one part of finely-divided *titaniferous schorl* with from 1 to 2 parts of carbonate of soda, and ½ to 1 part of sulphur is thrown into a red-hot crucible by small portions at a time, in proportion as the mass subsides. The whole is then kept at a moderate red heat for some time, whereby it is reduced to a pasty consistence. The resulting black mass, which has a jet-like lustre, and contains the greater part of the titanium in the state of titanous oxide, is powdered and diffused in boiled water; the liquid decanted; and the insoluble portion treated in the cold with dilute sulphuric acid, whereby the whole of the iron and a portion of the titanous oxide are dissolved. The latter is then precipitated from the solution by the cautious addition of carbonate of soda, while the protoxide of iron remains dissolved. The portion left undissolved by the dilute sulphuric acid, is gently heated with oil of vitriol; and a solution thus obtained, consisting of titanous oxide nearly free from iron. The portion not dissolved by the oil of vitriol is a mixture of carbon and titanic acid, which, after roasting, is obtained perfectly white and free from iron. It is better first to fuse the rutile with the carbonate of soda in a silver crucible, and afterwards the powdered mass with sulphur in a crucible lined with charcoal. (Berthier.)

4. A mixture of powdered rutile and carbonate of soda is exposed in a charcoal crucible to the heat of a blast-furnace; the black crystalline

cake broken up; and the powder passed through a sieve, which retains a quantity of granulated iron. The greater portion of the iron which has passed through the sieve, is separated by means of a magnet, and the rest is removed by concentrated hydrochloric acid, which at the same time dissolves a portion of titanous oxide, and acquires a wine-red colour. The residue insoluble in hydrochloric acid, is boiled with oil of vitriol, in which it dissolves completely, and the solution evaporated to dryness and ignited; titanic acid then remains, together with a trace of iron. (Berthier, *Ann. Chim. Phys.* 50, 304.)

5. Chloride of titanium prepared from rutile by the second method (III. 479) is dissolved in water, and the titanic oxide precipitated by ammonia and ignited.

*Properties.—Native Titanic Acid* occurs in two dimorphous states: a. *Rutile, Titaniferous Schorl.*—Crystalline system the square prismatic; *Fig.* 28, 29; *Fig.* 39, without the *p*-face, but with *a*-faces (of the second square-based octohedron), and having the lateral edges between *q* and *r*, replaced by planes (whereby a sixteen-sided prism is formed); also in other forms, especially hemitropic macle-crystals; $e : e' = 123° 4'$; $a : q = 122° 51'$; cleavage parallel to *q* and *r*. (Hauy.) Specific gravity = 4·249 (Mohs.) Softer than quartz. Translucent; brownish-red; yields a brownish-yellow powder.

b. *Anatase.*—Crystalline system the square prismatic. Acute square-based octohedrons. *Fig.* 21, frequently truncated (*p*-face), or accuminated with four faces. *Fig.* 22, $e : e' = 97° 38'$; $e : e^1 = 137° 10'$; $p : e = 111° 25'$; cleavage parallel to *e* and *p*. (Hauy.) Specific gravity = 3·826 (Mohs.) Harder than apatite. Translucent; blue, inclining to brown, red, and black; yields a greyish-white powder.

¶ *Brookite*, discovered by Soret and described by Levy, belongs to the right prismatic system; has precisely the colour and lustre of rutile; and, like that mineral, is insoluble in all acids except boiling oil of vitriol. Occurs in opaque crystals of specific gravity 4·167 ... 4·165; its density is increased by ignition. A specimen from Snowdon, analyzed by Rose, contained, besides titanic acid, only 1·41 per cent. of iron. (H. Rose.) ¶

*Artificial Titanic Acid.*—White powder, of specific gravity 3·9311; assumes a yellow colour when heated. When precipitated by ammonia and subsequently ignited, it appears, according to H. Rose, as a brownish solid mass, having a diamond lustre and resembling rutile.—Tasteless; reddens only that portion of tincture of litmus which it absorbs. (H. Rose.) Fuses only before the oxyhydrogen blowpipe.—[For its behaviour with fluxes, see page 486.]

¶ According to H. Rose (*Ann. Pharm.* 53, 267), titanic acid is susceptible of two modifications corresponding to those of the metal; (*vid.* Silicium, p. 352). $TiO^2\alpha$, is precipitated from solutions of titanic acid by ammonia, and is soluble in dilute acids, both in the moist state and after careful drying; moreover, its solution may be diluted with cold water without becoming turbid. It becomes incandescent when ignited. $TiO^2\beta$ is thrown down on boiling a solution of the acid in a stronger acid, (as the hydrochloric) and may also be obtained by igniting $TiO^2\alpha$. It is insoluble in all acids except boiling oil of vitriol, in which it dissolves slowly; does not emit light when ignited, and recovers its original whiteness on cooling. ¶

| | | | |
|---|---|---|---|
| Ti | 24 | ..... | 60 |
| 2O | 16 | ..... | 40 |
| $TiO^2$ | 40 | ..... | 100 |

$TiO^2 = 303{\cdot}66 + 200 = 503{\cdot}66$. (Berzelius.)

*Decompositions.*—1. By potassium or sodium at a red heat, with moderate incandescence; the product being potash or soda, and a black powder, which is not susceptible of metallic lustre, and appears to be a mixture of titanium and titanic acid [or titanous oxide?]. (H. Rose.)—2. By charcoal at a white heat, it is reduced to the metallic state.—3. With bisulphide of carbon, at a strong red heat, it yields carbonic acid, carbonic oxide, and sulphide of titanium. (H. Rose.)—Hydrosulphuric acid imparts a black colour to ignited titanic acid, but the blackness is removed by subsequent ignition in the air. (H. Rose.)—Hydrogen gas and carbonic oxide do not affect titanic acid at a red heat. According to Pfaff, the Norwegian rutile, when exposed to the oxy-hydrogen blowpipe-flame, fuses at first to a slag, and is then, apparently, reduced to a metallic globule. [iron ?].

*Combinations.*—*a.* With water: Hydrate of Titanic Acid.—Prepared by precipitating a solution of titanic oxide in an acid by means of an alkali, or by decomposing titanate of potash with hydrochloric acid.—White; and, when recently precipitated, flocculent and bulky; sometimes also rather gelatinous, especially when prepared by the second process. When washed with water, it passes through the filter in the form of a milky liquid, and at the same time clogs up its pores; this inconvenience however, does not occur if the water is mixed with an acid, an alkali, or a salt. The hydrate precipitated by boiling a dilute solution, becomes covered, while drying, with a brown shining film. (Rose.) The hydrate loses its water when heated, blackening at first and then emitting a feeble light. (Chevreul, *Ann. Chim. Phys.* 13, 249.) Whether the precipitated titanic acid contains anything more than hygroscopic water, and if so, what proportion, has not yet been determined; probably after drying it should be regarded as anhydrous, amorphous titanic acid, and only in the recently precipitated gelatinous state, as a hydrate.

¶ Titanic Acid precipitated by ammonia and dried in vacuo over oil of vitriol, consists of $TiO^2$, HO, together with a small quantity of ammonia, which cannot be removed by washing, and to the reducing action of which must be ascribed the blackness assumed by precipitated titanic acid on ignition. (H. Rose, *Ann. Pharm.* 53, 267.) ¶

*b.* With Acids: yielding the Salts of Titanic Oxide. The affinity of titanic oxide for acids is very feeble. Both the native crystallized oxide and the ignited artificial oxide, dissolve only in hydrofluoric acid, and when finely pounded, in boiling oil of vitriol. Hence a solution can only be obtained by digesting in the other acids, either the hydrated titanic acid or the acid titanate of potash which remains after fusing titanic oxide with carbonate of potash, and washing away the soluble portions with water. Solution is effected but slowly, much more rapidly and abundantly, however, by using concentrated acids either cold or very slightly warmed, than when hot dilute acids are employed. The titanic acid precipitated by ammonia and washed with cold water, dissolves the most readily; that which has been washed with hot water

less perfectly; and the precipitate obtained by boiling a dilute hydrochloric acid solution, least readily and completely of all. (H. Rose.)

The solutions are sometimes yellow, sometimes colourless, and have a very rough and acid taste. They yield on evaporation an amorphous residue, which, when the acid has escaped during the evaporation, no longer dissolves completely in water.—Tin, zinc, and iron immersed in acid solutions of titanic oxide, produce a blue colour at first, and afterwards throw down, from tin-solutions, a purple-red, and from zinc-solutions, a violet-coloured powder (of titanous oxide?) which appears reddish-brown by transmitted light, and after the lapse of a few days, is again converted into the white oxide. The hydrochloric acid solution, after being boiled for some time with copper, assumes a cherry-red colour, and then yields, on the addition of ammonia, a dark cherry-red precipitate, which, after a short time, is again converted into white titanic acid. (Fuchs, *J. pr. Chem.* 18, 495.)—Solutions of titanic oxide are decomposed at the boiling point, especially when they do not contain an excess of acid and are diluted with water, the oxide being precipitated in the form of a very insoluble basic salt. The smaller the excess of acid, the more complete is the precipitation. Sulphite of ammonia boiled with the salts till sulphurous acid ceases to be disengaged, precipitates the whole of the titanic oxide; the precipitate is free from sulphurous acid and easy to wash. (Berthier.) Phosphoric, sulphuric, arsenic, oxalic, and tartaric acid and their alkaline salts (but not nitric, acetic, or citric acid), added to a solution of titanic oxide in hydrochloric acid, made as neutral as possible, precipitate a white salt (more completely, however, when aided by heat), soluble in excess of hydrochloric acid, and likewise in an excess of the acid used for precipitation. The caustic alkalis, alkaline carbonates, and alkaline hydrosulphates give off carbonic acid or sulphuretted hydrogen, and throw down white gelatinous flakes of hydrate, which are slightly soluble in excess of the alkaline carbonates only. When iron is present, the precipitate produced by the alkaline hydrosulphate assumes a green or blue colour, from admixture of hydrated sulphide of iron. Ferrocyanide of potassium produces a dense orange-brown precipitate, soluble in excess of the reagent. If the solution contains sesquioxide of iron or a large excess of acid, the precipitate is coloured dark green, from formation of Prussian blue. Tincture of galls added in large quantity gives a dense brownish-red precipitate. Hydrosulphuric acid does not affect the salts of titanic oxide.

c. With Salifiable Bases: producing the Salts of Titanic Acid, or Titanates. Some of these compounds are found native, others are prepared by fusion, and others again in the wet way. When reduced to fine powder, they dissolve in moderately warm concentrated hydrochloric acid. Boiling dilute hydrochloric acid, on the contrary, precipitates the greater part of the titanic acid in the form of a white powder. They are mostly insoluble in water.

*Titanic oxide* does not appear to unite with carbonic acid.

### Titanium and Phosphorus.

A. Phosphide of Titanium.—By strongly igniting phosphate of titanium with charcoal and a small quantity of borax, Chenevix obtained a white, brittle, granular phosphide of titanium, fusible before the blowpipe.

B. Phosphite of Titanic Oxide.—An aqueous solution of chloride of titanium dissolved in water, is precipitated by an aqueous solution of terchloride of phosphorus neutralized with ammonia.—White precipitate, which, when ignited in a retort, evolves hydrogen gas mixed with vapour of phosphorus, and leaves a black residue, in which the titanic acid is not reduced to the state of titanous oxide. (H. Rose, *Pogg.* 9, 47.)

C. Phosphate of Titanic Oxide.—Precipitated on mixing phosphoric acid with the hydrochloric acid solution of titanic oxide, in white bulky flakes, which are soluble either in an excess of phosphoric acid or of the solution of titanium, and dry up to a shining, gummy mass. If the solution of titanium contains ferric oxide, the latter is completely precipitated together with the titanium. (H. Rose.)

## Titanium and Sulphur.

A. Sulphide of Titanium.—1. Titanic acid formed into lumps by moistening it and afterwards pressing and drying, is strongly ignited in a porcelain tube, and vapour of bisulphide of carbon, evolved by the application of a moderate heat from a retort attached to one end of the tube, is passed over it—the carbonic acid and undecomposed sulphide of carbon being conducted from the other end of the tube under water; the apparatus is then allowed to cool, and afterwards taken to pieces. A portion of the titanic acid is very apt to escape decomposition; some black sulphide of titanium, probably protosulphide, is also produced. (H. Rose.) 2. A mixture of one part of rutile with one part of dry carbonate of soda, one part of sulphur, and sometimes also $\frac{1}{2}$ pt. of charcoal, is strongly pressed into a crucible and covered with a stratum of charcoal; the whole is then strongly ignited, though not so long nor at so high a temperature as in the preparation of metallic titanium. (III., 467.) The dense, fused, black mass thus obtained, contains a great number of yellow scales of sulphide of titanium. The mass is coarsely pounded, digested with water, and the solution of sulphide of sodium decanted from the black residue. The latter is treated with oil of vitriol, which dissolves a large quantity of titanium, and the remaining sulphide of titanium purified with water. Should any black grains of titanous oxide be found mixed with it, the sulphide is once more fused with carbonate of soda and sulphur; if, however, the quantity of titanous oxide is but small, the sulphide of titanium, which is lighter, may be separated from it by levigation. (Berthier.) ¶ 3. When a mixture of bichloride of titanium and hydrosulphuric acid gas is passed through a red-hot tube, the tube becomes covered with a stratum of crystalline scales, having a brilliant metallic lustre and yellow colour, like mosaic gold. In moist air, they exhale a faint odour of hydrosulphuric acid; they are not soluble in hydrochloric or in dilute sulphuric acid, but dissolve in aqua-regia without appreciable residue. (Ebelmen, *Ann. Chim. Phys.* 20, 385.) ¶ Dark green mass, which becomes brazen-yellow by pressure; leaves a stain like talc; and when rubbed on the skin, imparts to it a brazen-yellow colour. (H. Rose.) Bronze-yellow scales, often of considerable breadth. (Berthier.)

| | | | | Ebelmen. |
|---|---|---|---|---|
| Ti ..... | 24 ..... | 42·86 ..... | 44·05 |
| 2S ..... | 32 ..... | 57·14 ..... | 56·40 |
| $TiS^2$ ..... | 56 ..... | 100·00 ..... | 100·45 |

When ignited in the air it burns readily, yielding titanic acid and sulphurous acid, which is volatilized. Detonates when heated with nitre. Decomposed when a current of dry chlorine gas is passed over it, the products being chloride of sulphur and chloride of titanium. Any titanic acid which may be mixed with the sulphide of titanium remains behind. With nitric acid it evolves heat, and is resolved, with disengagement of nitric oxide, into titanic acid and sulphur. It is oxidized by warm aqua-regia, yielding titanic acid (the greater part of which remains undissolved) and sulphuric acid. Dissolves slowly in hydrochloric acid, with evolution of hydrosulphuric acid. (H. Rose.) At a tolerably strong red heat, it decomposes vapour of water with great facility, and is converted into titanic acid, with disengagement of hydrosulphuric acid and a quantity of hydrogen gas. (Regnault.) [The free hydrogen is probably produced from the decomposition of the hydrosulphuric acid by heat; if so, sulphur must likewise be set free.] Digested with an aqueous solution of caustic potash, it is rapidly converted into white titanate of potash which is precipitated, and hydrosulphate of potash which dissolves:

$$TiS^2 + 2KO = TiO^2 + 2KS.$$

Not soluble in bi-hydrosulphate of potash. (H. Rose.)

B. Sulphite of Titanic Oxide.—Hydrated titanic oxide dissolves very sparingly in an aqueous solution of sulphurous acid, and is again completely precipitated on boiling. (Berthier.)

C. Sulphate of Titanic Oxide.—*a. Basic sulphate.*—A dilute solution of titanium in hydrochloric acid, is precipitated by sulphuric acid. (Sesquioxide of iron and potash remain dissolved in the liquid.) White; reddens moist litmus paper strongly. By ignition it is converted into pure titanic oxide. After drying it rapidly absorbs moisture. Dissolves in an excess of sulphuric acid, and also in an excess of the hydrochloric acid solution of titanium. (H. Rose.)

| | H. Rose. | | |
|---|---|---|---|
| Titanic oxide | 76·83 | to | 76·50 |
| Sulphuric acid | 7·78 | ,, | 7·56 |
| Water | 15·39 | ,, | 15·94 |
| | 100·00 | ,, | 100·00 |

When this salt is dissolved in excess of sulphuric acid, and the solution diluted with water or alcohol, a similar salt is precipitated, but containing variable proportions of its constituents; in one experiment, 73·55 per cent. of titanic oxide, 9·68 of sulphuric acid, and 16·77 of water were obtained. Probably a mixture of *a* and *b*. (H. Rose.)

*b. Acid sulphate.*—1. Titanic oxide reduced (if previously ignited) to fine powder, is digested with a mixture of one part of oil of vitriol and ½ pt. of water, till the whole of the water is expelled; the temperature is then raised—but not to redness—to drive off the excess of sulphuric acid; and the residue is dissolved in a small quantity of water. (Berzelius.) 2. Hydrated titanic oxide, basic titanic sulphate, or acid titanate of potash (in which case sulphate of potash is produced at the same time), is dissolved in moderately dilute sulphuric acid, an operation which requires considerable time. Colourless solution, from which, on diluting with water, (especially if heat be applied at the same time) or on adding alcohol, the compound *a*, containing however a somewhat

larger proportion of acid, is precipitated. (H. Rose.) ¶ By dissolving chloride of titanium in sulphuric acid, and evaporating the solution in vacuo over caustic lime, Ebelmen obtained an imperfectly crystallized mass having a violet colour. The solution became colourless on boiling, from separation of titanic acid. By analysis, Ebelmen obtained a quantity of sulphuric acid larger than that required by the formula, $Ti^2O^3, 3SO^3$. (Ebelmen, *N. Ann. Chim. Phys.* 20, 385.) ¶

## Titanium and Chlorine.

¶ A. Sesquichloride of Titanium.—Prepared by the action of hydrogen gas on bichloride of titanium at a high temperature. Small, dark violet-coloured scales, which, when heated in a platinum crucible in contact with air, evolve bichloride of titanium and leave a quantity of titanic oxide; a similar decomposition takes place at ordinary temperatures, but much less rapidly. This compound is much less volatile than the bichloride and deliquesces in the air. When dissolved in water, it is probably converted into $Ti^2O^3, 3HCl$. The solution is violet-red, but becomes colourless on exposure to the air, in consequence of the formation of titanic acid. With alkalis it yields a dark brown precipitate, quickly changing to black, then to blue, and lastly to white, with disengagement of hydrogen. With alkaline carbonates it behaves nearly in the same manner. Hydrosulphuric acid does not affect it; sulphide of ammonium acts like the caustic alkalis. Sesquichloride of titanium is a powerful reducing agent. Sulphurous acid is reduced when heated with it, sulphur being deposited. Gold, silver, and mercury are precipitated by it from their solution, in the metallic state; and salts of ferric oxide are reduced to salts of ferrous oxide. When evaporated to dryness, it evolves hydrochloric acid, and leaves a blue oxy-chloride of titanium. Besides the sesquichloride and a small quantity of metallic titanium, the above process likewise yields golden-yellow scales, which Ebelmen is disposed to regard as *Protochloride of Titanium*. (*N. Ann. Chim. Phys.* 20, 385.) ¶

| | Calculation. | | | | Ebelmen. | | | |
|---|---|---|---|---|---|---|---|---|
| 2Ti | 48·0 | .... | 31·3 | .... | 32·3 | .... | 31·6 | |
| 3Cl | 96·2 | .... | 68·7 | .... | 67·9 | .... | 67·2 | |
| $Ti^2Cl^3$ | 144·2 | .... | 100·0 | .... | 100·2 | .... | 98·8 | |

B. Bichloride of Titanium.—1. Chlorine gas dried by means of chloride of calcium, is passed over titanium ignited in a glass tube (in the cold, no effect is produced). The chloride of titanium condenses in the cooler part of the tube. (George, *Ann. Phil.* 25, 18; also *Schw.* 44, 48; and *Pogg.* 3, 171.)—2. Dry chlorine gas is passed over a red-hot mixture of titanic acid and charcoal. For this purpose, powdered rutile may be used, because the liquid chloride of titanium can be separated by decantation or distillation from the fixed chloride of iron which is produced at the same time. (Dumas, *J. Pharm.* 12, 300; also *Pogg.* 7, 532; also *Ann. Chim. Phys.* 33. 386.) Even the heat of an argand spirit-lamp is sufficient. (Wöhler.) To free the chloride of titanium from excess of chlorine, which gives it a yellow colour and also the property of discharging vegetable colours after dilution with water, it is agitated with small quantities of mercury and distilled two or three times in a small retort containing mercury. (Dumas.) H. Rose rectifies it four or five times from mercury or potassium.

Transparent, colourless, very dense liquid. Boils at 135° when the barometer stands at 0·763 metres (30 inches), and yields a vapour of specific gravity 6·836. (Dumas.) Has a pungent, acid odour, and emits dense white fumes in the air.

| | | | H. Rose. | | | Volume. | Sp. gr. |
|---|---|---|---|---|---|---|---|
| Ti ..... | 24·0 | 25·32 | 25·54 | Vapour of titanium | | 1 | 1·6632 |
| 2Cl ..... | 70·8 | 74·68 | 74·46 | Chlorine gas ..... | | 2 | 4·9086 |
| $TiCl^2$ .... | 94·8 | 100·00 | 100·00 | | | 1 | 6·5718 |

It is not decomposed by potassium at its boiling point; but if its vapour is passed over heated potassium or sodium, the titanium is reduced with so violent a disengagement of light and heat, that the tube actually fuses at the point where the action takes place. (H. Rose.)

*Hydrochlorate of Titanic Oxide.*—1. Formed by mixing bichloride of titanium with water. The combination is attended with very great rise of temperature.—2. Hydrated titanic oxide (even that which has been precipitated by boiling), or acid titanate of potash (in which case a small quantity of chloride of potassium is formed), is dissolved in concentrated hydrochloric acid. By the first method, provided only a very small quantity of water be used, the salt may be obtained in a solid state. (George.) The second method yields a yellow liquid, which, by careful evaporation, may be freed from excess of hydrochloric acid. When the solution is evaporated to dryness, a residue remains, which, according to Chevreul, leaves, on being again treated with water, a large quantity of titanic oxide no longer soluble in hydrochloric acid. When still further heated, the oxide loses the whole of its acid. The hydrochloric acid solution of titanic oxide diluted with three times its bulk of water, yields, even at a temperature below its boiling point, a deposit of basic hydrochlorate of titanium. The same precipitate is obtained at ordinary temperatures after standing for several months. (Chevreul.)

C. Chloride of Titanium with Phosphuretted Hydrogen.—Phosphuretted hydrogen gas, either of the more or the less inflammable variety, after being dried by passing over chloride of calcium, is brought in contact with purified chloride of titanium in a close vessel. The chloride absorbs the gas and is first converted into a greasy yellow substance; but when completely saturated—for which purpose a large quantity of gas is required—it forms a solid brown mass which fumes on exposure to the air. No hydrochloric acid is set free during the process. The brown compound, when heated in a close vessel, evolves hydrochloric acid gas, and a small quantity of phosphuretted hydrogen (the latter especially, if it had been previously saturated with the gas as much as possible), and sublimes in the form of a lemon-yellow substance (to be described under D), with which a portion of free phosphorus is likewise mixed; a copper-coloured residue is left, consisting of metallic titanium. From the presence of air and moisture, however, a small quantity of titanic oxide blackened with metallic titanium is likewise produced. The brown compound is decomposed by water, by aqueous hydrochloric acid, and by the aqueous solutions of caustic potash and ammonia or their carbonates, evolving phosphuretted hydrogen gas with effervescence. Water and hydrochloric acid form a solution of hydrochlorate of titanium; the alkalis precipitate titanic oxide. Whether the compound has been prepared with the more inflammable or with the less inflammable phosphuretted hydrogen, the gas, disengaged by the above-mentioned re-agents,

—with the exception of caustic ammonia, which evolves spontaneously inflammable phosphuretted hydrogen—is always of the non-spontaneously inflammable variety. Consequently the less inflammable gas may be rendered spontaneously inflammable by combining it with chloride of titanium and afterwards setting it free by ammonia; and the spontaneously inflammable gas converted into the less inflammable variety by disengaging it with water, &c. Ammoniacal gas, being a more powerful base, expels the phosphuretted hydrogen gas from the brown compound, even in the cold, converting it, at least for the most part, into chloride of titanium and ammonium. (H. Rose.)

C. Chloride of Titanium with Hydrochloric Acid and Phosphuretted Hydrogen.—The lemon-yellow substance sublimed by heating B. When sublimed, or when treated with water, hydrochloric acid, or the alkalis, it exhibits the same characters as B, but has a different composition. (H. Rose.)

| | Calculation. | | | H. Rose. |
|---|---|---|---|---|
| $PH^3$ | 34·4 | .... | 9·69 | |
| HCl | 36·2 | .... | 10·19 | |
| 3Ti | 72·0 | .... | 20·29 | .... 20·47 |
| 6Cl | 212·4 | .... | 59·83 | .... 68·38 |
| $PH^3, HCl + 3TiCl^2$ | 355·0 | .... | 100·00 | |

The 68·38 parts of chlorine, found by Rose, belong to the chloride of titanium and the hydrochloric acid together.

D. Chloride of Sulphur and Titanium.—1. A mixture of chloride of titanium and chloride of sulphur yields at ordinary temperatures splendid, large, yellow crystals.—2. Chlorine gas is passed over sulphide of titanium. The sulphide first deliquesces to a yellow liquid, which is probably a compound of chloride of titanium with a chloride of sulphur containing less than 2 atoms of sulphur. After absorbing more chlorine, the liquid solidifies to an indistinctly crystalline, pale yellow substance, which melts at a gentle heat, and again becomes crystalline on cooling; sublimes undecomposed when gently heated; and emits dense white fumes in the air. It contains one atom of $TiCl^2$ combined in variable proportions with less than one atom of $SCl^2$.

$TiS^2$, when decomposed by chlorine, should yield one atom of chloride of titanium to every 2 atoms of chloride of sulphur; but the principal part of the latter appears to pass off with the chlorine. Rose found that at a moderate heat the compound evolved chloride of sulphur, while the residue still continued solid. The four following specimens examined by Rose were prepared at different times. The specimen *c* was sublimed several times in a current of chlorine gas, by which means a larger quantity of chloride of sulphur was volatilized.

| | *a.* | *b.* | *c.* | *d.* |
|---|---|---|---|---|
| Ti | 15·58 | .... 17·73 | .... 20·87 | .... 19·56 |
| S | 9·08 | .... 6·23 | .... 3·70 | .... 4·08 |
| Cl | 75·34 | .... 76·31 | .... 75·58 | .... 77·31 |
| | 100·00 | .... 100·27 | .... 100·15 | .... 100·95 |

The compound deliquesces rapidly in the air, and its solution in water contains titanic oxide, hydrochloric acid, sulphuric acid, and hyposulphurous acid. It dissolves completely in dilute nitric acid with evolution of

red fumes, and yields a solution which contains titanic oxide, hydrochloric acid, and sulphuric acid, but no hyposulphurous acid. Fuming nitric acid converts it into a thick white mass which dissolves completely in water. (H. Rose.)

## Titanium and Fluorine.

A. Fluoride of Titanium and Bi-hydrofluate of Titanic Oxide.—When titanic oxide is distilled in a leaden retort with fluorspar and oil of vitriol, no gas is evolved, but after a considerable time some yellow oleaginous drops (fluoride of titanium?) appear, which are decomposed by water, with separation of titanic oxide (or of B?). If a glass retort is used, gaseous fluoride of silicium passes over mixed with fluoride of titanium. (Unverdorben, *N. Tr.* 9, 1, 32.)

By evaporating terhydrofluate of titanic oxide at a gentle heat, a syrupy liquid is obtained, from which crystals of the bihydrofluate separate. These crystals are resolved by water into terhydrofluate of titanic oxide which dissolves in the liquid, and the insoluble basic salt B. (Berzelius.)

Fluoride of titanium enters into combination with other metallic fluorides, forming compounds called Titano-Fluorides, which, in the state of solution, may likewise be considered as *hydrofluates of titanic oxide and another base.* They are prepared by dissolving a salifiable base in terhydrofluate of titanic oxide, and afterwards evaporating the solution. They contain one atom of bifluoride of titanium combined with one atom of another metallic fluoride. (Berzelius.) The potassium compound, for instance, consists of $KF, TiF^2$, and when in solution may be regarded as $KO, HF + TiO^2, 2HF$. The titano-fluorides sustain a red heat without decomposition.

B. Oxy-fluoride of Titanium.—The white powder precipitated in the decomposition of crystallized bihydrofluate of titanic oxide by water. It does not part with its fluorine at a red heat. The fluorine can only be expelled by projecting carbonate of ammonia into the ignited crucible containing the salt. (Berzelius.)

C. Ter-hydrofluate of Titanic Oxide.—*Hydrofluotitanic Acid.*—Corresponds to the terhydrofluate of silica or hydrofluosilicic acid. $TiF^2 + HF$ or $TiO^2 + 3HF$. Known only in solution. Formed by the decomposition of the crystallized bihydrofluate of titanic oxide with water; or by dissolving titanium in a warm mixture of hydrofluoric acid and nitric acid, or of titanic oxide in aqueous hydrofluoric acid. In the latter case, the oxide becomes heated on the addition of the hydrofluoric acid, and, after long digestion, is completely dissolved. (Berzelius, *Pogg.* 41.)

*Warwickite.*—Belongs to the right prismatic system; *Fig.* 61, with the edge between $u^1$ and $u$ (the $m$-face) replaced by a plane; $u' : u = 93°$.... 94°. Cleavage parallel to $t$. Specific gravity from 3·0 to 3·14. Brown inclining to black. At the thin edges it appears translucent and of a reddish brown colour. Warwickite contains 64·71 per cent. of titanium, 7·14 of iron, 0·80 of yttrium, and 27·33 of fluorine, with a trace of alumina. (Shepard, *Sill. Amer. J.* 34, 313; 36, 85.) Hence it must contain $Ti^2F$. This mineral must not be confounded with *Varvicite*, (*Vid.* Manganese, Chapter XXIII.)

### Titanium and Nitrogen.

A. Nitrate of Titanic Oxide.—Prepared by dissolving hydrated titanic oxide or acid titanate of potash in nitric acid.

B. Titanate of Ammonia?—When ammonia is added to the milky mixture of hydrated titanic acid and water, a coherent flocculent precipitate is formed, which can be easily washed on the filter. (H. Rose.)

C. Carbonate of Titanic Oxide and Ammonia.—When an acid solution of titanium is dropped into a large excess of carbonate of ammonia dissolved in water, the resulting precipitate is redissolved, and on boiling the liquid, titanic oxide is thrown down. (Berzelius.)

D. Ammonio-Chloride of Titanium. — When ammoniacal gas dried by means of hydrate of potash, is passed over chloride of titanium, it is rapidly absorbed with great evolution of heat. The current of ammoniacal gas must, however, be kept up for a long time, and the mass frequently stirred in order to ensure that the whole of the chloride—which otherwise becomes partially enveloped by the new compound—may be saturated with ammonia. The product must be rapidly enclosed in dry, well stopped bottles. If the compound still smells of ammonia when the bottles are opened after some time, it may be considered to be thoroughly saturated; otherwise it evolves a white cloud, and must be again treated with ammonia. Brownish red powder. (H. Rose.) Pale yellow. (Persoz.)

| | | | H. Rose. | Persoz. |
|---|---|---|---|---|
| $2NH^3$ | 34·0 | 26·40 | 25·08 | 34·14 |
| Ti | 24·0 | 18·63 | 19·22 | 65·86 |
| 2Cl | 70·8 | 54·97 | 55·70 | |
| $2NH^3, TiCl^2$ | 128·8 | 100·00 | 100·00 | 100·00 |

According to the analysis of Persoz, it consists of $3NH^3, TiCl^2$.

When this compound is heated in a glass tube, it first evolves a small quantity of ammoniacal gas, provided it has previously been completely saturated with ammonia—then a portion of sal-ammoniac—then a quantity of hydrochloric gas, doubtless accompanied by nitrogen,—and yields, besides a residue of metallic titanium, a yellowish white sublimate, which is found to be a compound of chloride of titanium with hydrochlorate of ammonia, and is acid only from adhering hydrochloric acid. If the compound has absorbed moisture from the air and thereby become white, it leaves titanic acid instead of metallic titanium when heated in a glass tube, and yields a sublimate of sal-ammoniac. The anhydrous compound is decomposed with vivid incandescence by heated potassium or sodium. (III., 468.) It absorbs moisture greedily, becomes white, and deliquesces in a very moist atmosphere; with water it yields a solution which is not perfectly transparent. $2NH^3, TiCl^2$ with $2HO$ should form $2(NH^3, HCl) + TiO^2$, the sal-ammoniac being dissolved, and the whole of the titanic oxide precipitated. The quantity of titanic oxide actually precipitated is, however, very small; and the precipitation is not complete even on the addition of ammonia; which, together with the fact that bichloride of platinum precipitates from the solution only half the ammonia—indicates that the ammonio-chloride of titanium dissolves in water without decomposition, and not as a mixture of sal-ammoniac and titanic oxide. (H. Rose.)

E. Chloride of Titanium with Sal-ammoniac, or Chloride of Titanium and Ammonium.—This is the yellowish white sublimate obtained by heating D in a glass tube. When sublimed a second time, it exhibits the same decompositions as D. Dissolves in water without turbidity. Appears to contain sometimes $1\frac{1}{2}$ At. sometimes 3 At. of sal-ammoniac, according to the manner in which it has been prepared—and more especially according to the number of sublimations to which it has been subjected. (H. Rose.)

| | | | | | H. Rose. |
|---|---|---|---|---|---|
| $3NH^3$ | 54·0 | | 15·44 | | |
| 2Ti | 48·0 | | 13·72 | | 13·68 |
| 7Cl | 247·8 | | 70·84 | | 69·68 |
| $3NH^4Cl, 2TiCl$ | 349·8 | | 100·00 | | |

| | | | | | H. Rose. |
|---|---|---|---|---|---|
| $3NH^4$ | 54 | | 21·18 | | |
| Ti | 24 | | 9·41 | | 9·30 |
| 5Cl | 177 | | 69·41 | | 68·34 |
| $3NH^4Cl, TiCl$ | 255 | | 100·00 | | |

F. Fluoride of Titanium with Hydrofluate of Ammonia, or Fluoride of Titanium and Ammonium.—a. *In equal numbers of atoms.* —$NH^4F, TiF^2$.—Formed by adding ammonia to terhydrofluate of titanium till the titanic oxide which is precipitated ceases to redissolve, and evaporating the solution to the crystallizing point.—Brilliant scales.—When distilled in a platinum vessel, at a temperature considerably below redness, it yields, without fusing, a sublimate of hydrofluate of ammonia, and leaves *b*.

b. *With excess of Fluoride of Titanium.*—Probably $NH^4F, 2TiF^2$.—This substance fuses at an incipient red heat, and sublimes unchanged in amorphous flakes, which are soluble in water and have a rough, acid taste. A large excess of potash is required to precipitate the whole of the titanic oxide; and after the precipitation, the liquid smells of ammonia. (Berzelius.)

## Titanium and Potassium.

A. Titanate of Potash.—*a. With excess of Potash.*—Hydrated titanic oxide and the titanates of potash, *b* and *c*, are slightly soluble in excess of caustic potash. (Vauquelin, Rose.) The precipitate produced on dropping hydrochlorate of titanic oxide into an excess of potash, redissolves in the latter; dilute sulphuric acid causes reprecipitation. (Wöhler.)

*b. Monotitanate.*—One atom of titanic acid fused with excess of carbonate of potash, appears to expel one atom of carbonic acid. Two fluid strata form in the crucible; the upper stratum consists of the excess of carbonate of potash, which remains undecomposed and contains but a trace of titanic acid; the lower is monotitanate of potash.—If the fusion is arrested before the action has ceased, the carbonic acid still evolved from the interior of the mass forces its way with a cracking noise through the hardening surface, and renders it uneven. From an aqueous solution of carbonate of potash titanic acid does not expel carbonic acid. (H. Rose.) Titanic acid yields the same compound when fused with hydrate of potash as when fused with its carbonate. By boiling titanic acid with

solution of caustic potash, a white bulky compound is formed (according to Vauquelin), which may consist either of *b* or *c* in the hydrated state.

Monotitanate of potash forms a yellowish fibrous mass, more fusible even than carbonate of potash.—Titanic acid, fused in atomic proportion with carbonate of potash before the blowpipe, yields a transparent yellow bead, which, on cooling, crystallizes to a dark grey glass, and in so doing again becomes red-hot. (Berzelius, *Lehrbuch.*)—The salt is resolved by water into the salt *a* which dissolves, and hydrated acid titanate of potash which remains behind.

*c. Acid Titanate.*—Obtained in the hydrated state by decomposing *b* with water, and afterwards washing till the water begins to pass milky through the filter. Soft white powder, which, like hydrated titanic oxide, diffuses itself through water in a very finely-divided state, and in this state passes through the filter. After ignition, it contains from 17·33 to 18·01 per cent. of potash combined with 82·67...81·99 of titanic acid. (H. Rose.)

*d. Hypertitanate.*—The salt *c* is treated with concentrated hydrochloric acid and the mixture supersaturated with ammonia and then filtered. The precipitate, after ignition, contains 8·7 per cent. of potash with 91·3 of titanic acid. (H. Rose.)

B. Carbonate of Titanic Oxide and Potash.—Prepared like the double carbonate of titanic oxide and ammonia; in this case, however, the oxide is not precipitated by ebullition alone, but only by boiling with sal-ammoniac. (Berzelius, *Lehrbuch.*)

C. Sulphate of Titanic Oxide and Potash.—Titanic oxide dissolves in melted bisulphate of potash, yielding a transparent glass. Water renders the glass milk-white, and separates the greater part of the titanic oxide. The dissolved portion may be precipitated by ammonia. (Wöhler, *Pogg.* 7, 423.)

D. Fluoride of Titanium and Potassium and Hydrofluate of Titanic Oxide and Potash.—Potash is added to terhydrofluate of titanic oxide till a permanent precipitate begins to form. The liquid, on cooling, deposits scales which resemble boracic acid, and when dried become milk-white and exhibit a silky lustre. On exposure to heat, the scales give off small quantities of hygroscopic water and fluoride of titanium, and fuse at a white heat, without undergoing any further change. When heated with potassium, the salt is decomposed with vivid incandescence, yielding titanium and fluoride of potassium. Bisulphate of potash fused with it, separates only a small portion of fluoride of titanium. It dissolves readily in water, without decomposition. Contains 38·7 per cent. of potash, 35·0 of titanic oxide, and 26·3 of hypothetically anhydrous fluoric acid. (Berzelius.)

## Titanium and Sodium.

A. Titanate of Soda.—*a. Monotitanate.*—100 parts of titanic acid fused with from 5 to 12 times its weight of dry carbonate of soda, disengages between 46·18 and 50·96 parts of carbonic acid. (H. Rose.) [As one atom of $TiO^2$=40, and one atom of $CO^2$=22, (40 : 22=100 : 55) 100 parts of titanic acid should expel 55 parts of carbonic acid.]—An under stratum of monotitanate of soda is formed in the crucible,

and an upper stratum, consisting of undecomposed carbonate.—Monotitanate of soda, when treated with water, is resolved into soda which dissolves in the liquid, and insoluble hydrated acid titanate of soda. (H. Rose.)—Before the blowpipe, titanic oxide dissolves in carbonate of soda with effervescence, yielding a glass which is dark-yellow while hot—greyish white when cold, and is not absorbed by the charcoal. If the quantity of soda is just sufficient to retain the whole of the titanic oxide in solution at ordinary temperatures, the glass becomes crystalline at the very moment when it ceases to glow, and thereby evolves so much heat, that it again becomes red-hot and continues so for some time. (Berzelius.)

*b. Acid Titanate.*—Prepared by decomposing *a* with water and afterwards washing the precipitate till the water begins to pass milky through the filter. Small, white, sandy grains, containing from 15·14 to 15·30 per cent. of soda, from 74·73 to 75·47 of titanic acid, and from 10·13 to 9·23 of water. (H. Rose.)

*c. Hypertitanate.*—The salt *b* is first treated with concentrated hydrochloric acid, then with excess of ammonia, and filtered. A compound remains, containing between 3·8 and 3·44 per cent. of soda, and between 96·2 and 96·56 of titanic acid. (H. Rose.)

B. Carbonate of Titanic Oxide and Soda.—Prepared in the same manner as the double carbonate of titanic oxide and potash.

C. Before the blowpipe titanic oxide dissolves in borax, yielding a colourless or yellowish glass, which becomes milk-white by slight flaming, or—if it contains a larger quantity of the oxide—by mere cooling. In the deoxidizing flame it acquires a bluish purple colour. When it contains a larger quantity of titanic oxide and is exposed to the reducing flame on charcoal, it becomes dark yellow while hot, and blackish blue on cooling; by subsequent flaming it is rendered light blue and opaque; inasmuch as the titanous oxide formed imparts a reddish blue colour, and the remaining titanic oxide renders the glass white and opaque. (Berzelius.)

D. The glass which titanic oxide yields with microcosmic salt in the exterior blowpipe flame is colourless or yellowish; after long exposure to the reducing flame on charcoal (the reduction is promoted by the addition of a small quantity of tin) it appears yellowish while hot, and becomes violet blue on cooling. If the quantity of titanic oxide is very large, the blue colour thus produced is so dark that the glass becomes opaque, without however forming an enamel. The presence of iron changes the reddish blue colour into red. (Berzelius.)

E. Fluoride of Titanium and Sodium and Hydrofluate of Titanic Oxide and Soda.—Indistinct crystals, forming a saline crust; much more soluble in water than the potash compound. (Berzelius.)

## Titanium and Calcium.

*Perowskite*, which is found crystallized in cubes, contains titanic acid and lime. (G. Rose.)

FLUORIDE OF TITANIUM AND CALCIUM AND HYDROFLUATE OF TITANIC OXIDE AND LIME.—Carbonate of lime is dissolved in terhydrofluate of titanic oxide and the solution evaporated to a small bulk.—Prismatically formed crystals, which dissolve without alteration in acidulated water, but are decomposed by pure water, yielding an acid solution, and a white powder which contains an excess of fluoride of calcium. (Berzelius.)

## TITANIUM AND MAGNESIUM.

FLUORIDE OF TITANIUM AND MAGNESIUM AND HYDROFLUATE OF TITANIC OXIDE AND MAGNESIA.—Crystallizes by spontaneous evaporation in long needles, which have a bitter taste, are decomposed by pure water, and dissolve completely in acidulated water. (Berzelius.)

## TITANIUM AND ZIRCONIUM.

TITANATE OF ZIRCONIA.—Precipitated from a mixture of hydrochlorate of zirconia and hydrochlorate of titanic oxide on the addition of sulphate of potash. (Berzelius.)

*Polymignite.*—Crystalline system the right prismatic, *Fig.* 61, especially with the *m* and *a*-faces. Specific gravity = 4·8. Harder than felspar. Infusible before the blowpipe. Decomposed by oil of vitriol. (Berzelius.)

*Aeschynite.*—Crystalline system the right prismatic, *Fig.* 67, with *i*-faces; $u' : u = 127°$; $u : t = 116°$; $u : a = 169°$; $t : i = 143°$ or nearly so. Specific gravity = 5·14. (Brooke.) When heated it evolves water and traces of hydrofluoric acid. Swells up before the blowpipe, and fuses, at the edges only, to a black slag. (Hartwall.)

| *Polymignite*, according to Berzelius. | | *Aeschynite*, according to Hartwall. | |
|---|---|---|---|
| CaO | 4·20 | CaO | 3·8 |
| YO | 11·50 | ZrO | 20·0 |
| ZrO | 14·14 | $Ce^2O^3$ | 15·0 |
| $Ce^2O^3$ | 5·00 | $Fe^2O^3$ | 2·6 |
| $Mn^2O^3$ | 2·70 | $TiO^2$ | 56·0 |
| $Fe^2O^3$ | 12·20 | $SnO^2$ | 0·5 |
| $TiO^2$ | 46·30 | | |
| KO, MgO, $SiO^2$, $SnO^2$ | traces | | |
| | 96·04 | | 97·9 |

## TITANIUM AND SILICIUM.

A. TITANATE AND SILICATE OF POTASH.—Remains behind when titanic oxide is ignited with excess of silica and carbonate of potash, after the carbonate and silicate of potash have been washed out with water. While still moist, it is very soluble in concentrated hydrochloric acid, yielding a solution which, when diluted and boiled, becomes covered with a constantly renewed film, and deposits flakes which are rather soluble in water. Ammonia added to the solution precipitates a mixture of silica and titanic oxide, and the precipitate, after drying at a gentle heat, yields titanic oxide to concentrated hydrochloric acid. (H. Rose.)

B. Titanate and Silicate of Lime.—*Titanite, Sphene.*—Crystalline system the oblique prismatic. Primary form: *Fig.* 81, with numerous modifications; $u' : u = 133° 48'$; $p$ : the edge between $u'$ and $u = 127° 39'$. Cleavage parallel to $p$ and $u$. (G. Rose.) Specific gravity from 3·5 to 3·6. Harder than apatite. Transparent, iridescent. Before the blowpipe it swells up slightly and fuses at the edges to a dark glass. Dissolves with tolerable facility in borax, forming a transparent yellow glass in which the colour of the titanium (III., 486, C) does not appear. Dissolves with difficulty in microcosmic salt, the undissolved portion becoming milk-white; in the inner flame, the glass acquires the colour which is characteristic of titanium, more readily however on the addition of tin. With carbonate of soda it yields a turbid glass. (Berzelius.) It is decomposed by hydrochloric acid, which separates silica in a bulky form and containing titanic acid—the lime, together with a portion of the titanic acid, being dissolved.

| | | | | Klaproth. Passau. | Cordier. St. Gothard. |
|---|---|---|---|---|---|
| $3CaO$ | 84 | 32·68 | | 33 | 32·2 |
| $3SiO^2$ | 93 | 36·19 | | 35 | 28 0 |
| $2TiO^2$ | 80 | 31·13 | | 33 | 33·3 |
| $CaO,3SiO^2 + 2(CaO,TiO^2)$? | 257 | 100·00 | | 101 | 93·5 |

*Mosandrite.*—Consists principally of titanic acid, silicic acid, protoxide of cerium, and oxide of lanthanum, together with potash, lime, magnesia, and water.

### Other Compounds of Titanium.

Vauquelin and Hecht did not succeed in alloying titanium with arsenic, lead, copper, or silver; neither did Walchner succeed in alloying it with tin, lead, copper, or silver. According to Berzelius (*Pogg.* 1, 221), titanium, in combination with other metals, is oxidized and dissolved by acids; whereas, when pure, it withstands their action.

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Note to page 466.—Wöhler has lately shown that the copper-coloured crystals of titanium, which occur pretty frequently in the slags of blast-furnaces, and have hitherto been supposed to consist of metallic titanium, are really composed of cyanide and nitride of titanium. They contain 18 per cent. of nitrogen and 4 per cent. of carbon, and are represented by the formula:

$$Ti,C^2N + 3Ti^3N \quad \text{or} \quad TiCy + 3Ti^3N.$$

The titanium obtained by Rose's method (*p.* 468) is likewise a nitride of titanium, $Ti^3N^2$, containing 28 per cent. of nitrogen. (*Compt. rend.*, Nov. 5, 1849.)

END OF VOL. III.

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# ANNUAL REPORT

OF THE

# PROGRESS OF CHEMISTRY,

## And the Allied Sciences,

PHYSICS, MINERALOGY, AND GEOLOGY;

*Including the applications of Chemistry to Pharmacy, the Arts and Manufactures:*


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## Prospectus.

THE great and daily increasing number of researches appearing every year in the different departments of Chemistry and the Allied Sciences, renders it difficult for individuals to obtain, by actual inspection of the original sources, a complete survey of their progress.

The study of *one*, or even of several journals, does not suffice for this purpose, the communications of various investigators being distributed over a large number of periodicals, and many papers, especially interesting to the Chemist, being actually buried in publications chiefly devoted to other subjects.

It is evident that a rapid acquirement of an accurate knowledge of the progress made by so extensive a Science as Chemistry, and a clear per-

ception of the connexion of the individual researches as to their confirmation, correction, or refutation of each other, would be most materially facilitated by an Annual Report, founded on the broadest possible scientific basis, and carried out by men equal to the task.

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The labours in the field of Chemistry, including its application to Pharmacy, the Arts and Manufactures, will be reported with minute accuracy, it being intended to insert a faithful, and, whenever necessary, a complete digest of each investigation.

The part of the work devoted to Physics and Mineralogy will form a complete synopsis of the literature; while a detailed account will be given of such subjects as are of particular importance to the Chemist.

In Geology, which has of late derived so many advantages from the progress of Chemistry, the discussion will be extended to all inquiries instituted on the boundary line of the two Sciences.

The Annual Report aims at completeness, principally in the communication of *results;* descriptions, however, of *methods,* by means of which these results may have been obtained, will be by no means omitted, whenever it may appear conducive to the comprehension of the subject or whenever the methods themselves are new.

One of the principal objects will be to treat synoptically of the different researches published on the same subjects, and to expose in a lucid manner the relation existing between recent inquiries, and our actual store of knowledge; it is not intended to give merely isolated and unconnected abstracts of the several individual investigations.

By experience and researches of their own, the Authors of the Annual Report will be frequently enabled to point out such questions as require confirmation or correction, or to which, up to the present moment, due attention has not been accorded: criticism likewise cannot altogether be excluded.

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The Volumes for 1847 and 1848 will appear in Five Parts demy 8vo.

*Part IV., Organic Chemistry, will appear in December.*

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